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The Journal *of the* Society of Dyers and Colourists

Volume 75 Number 12

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FORTHCOMING MEETINGS OF THE SOCIETY

Tuesday, 12th January 1960

NORTHERN IRELAND SECTION. *Radio-isotopes and Their Industrial Applications.* R. J. Magee, Esq., M.Sc., Ph.D., M.R.S.A., A.R.I.C. (Queen's University, Belfast). Grosvenor Rooms, **Belfast.** 7.30 p.m.

SCOTTISH JUNIOR BRANCH. *Principles of Management.* W. A. Gray, Esq., B.Sc., A.R.C.S.T., A.M.B.I.M. (Senior Lecturer in Industrial Administration, Royal College of Science and Technology). Technical College, **Paisley.** 7.30 p.m.

Thursday, 14th January 1960

WEST RIDING SECTION. *Experience gained in the Dyeing and Finishing of Polyester/Wool Fabrics in Germany.* Dr. J. Nusslein (Farbwerke Hoechst). Victoria Hotel, Bridge Street, **Bradford 1.** 7.30 p.m.

MANCHESTER JUNIOR BRANCH. *A Survey of Modern Textile Finishing.* G. Landells, Esq., B.Sc., Ph.D., A.R.I.C., F.S.D.C. Room J/E 11, Chemical Engineering Building (Jackson Street), College of Science and Technology, **Manchester.** 4.30 p.m.

Friday, 15th January 1960

MANCHESTER SECTION. *Wool the Modern Fibre—A review of recent developments in the Wool Research Field.* Dr. E. G. Carter (International Wool Secretariat). Room C.2, College of Science and Technology, **Manchester.** 7.0 p.m.

Monday, 18th January 1960

BRADFORD JUNIOR BRANCH. *Problems in the dyeing of Wool, Fibro and Terylene for blending.* Miss Esmée Smith (Wm. Smith & Co. Ltd.) Institute of Technology, **Bradford.** 7.15 p.m.

Tuesday, 19th January 1960

HUDDERSFIELD SECTION. *Problems in Dyeing Polyester Fibres and Means of Overcoming Them.* Dr. J. Nusslein (Farbwerke Hoechst A.G.). Silvios Cafe, Westgate, **Huddersfield.** 7.30 p.m.

LEEDS JUNIOR BRANCH. *Mechanism of Dyeing with Procion Dyes.* H. H. Sumner, Esq., B.Sc. (I.C.I. Ltd.). The Lecture Theatre, Department of Colour Chemistry and Dyeing, the University, **Leeds 2.** 3.30 p.m.

MIDLANDS SECTION. *Beam Dyeing.* (Paper written by Burlington Corp. U.S.A.) K. S. Laurie, Esq. A.M.I.Mech.E., A.M.I.E.E. Gas Theatre, **Nottingham.** 7 p.m.

SCOTTISH SECTION. *Some Problems on the Dyeing and Finishing of Fabrics using the Newer Synthetics from the point of view of the customer.* J. S. Ingham, Esq., M.Sc., F.R.I.C. (Marks & Spencer Ltd.). St. Enoch Hotel, **Glasgow.** 7.15 p.m.

Friday, 22nd January 1960

WEST RIDING SECTION. Annual Dinner and Dance.

Thursday, 28th January 1960

WEST RIDING SECTION. *Levelling Agents for Wool Dyeing.* Dr. J. Lanter (CIBA, Basle). Victoria Hotel, Bridge Street, **Bradford 1.** 7.30 p.m.

Friday, 29th January 1960

HUDDERSFIELD SECTION. Annual Dinner. Princess Cafe, **Huddersfield.**

Saturday, 30th January 1960

MANCHESTER SECTION. Annual Dinner and Dance. Grand Hotel, **Manchester.** 6 p.m. for 6.30 p.m.

Monday, 1st February 1960

HUDDERSFIELD SECTION. *Choice of an Artificial Daylight for Colour Matching with Special Reference to Fluorescent Materials.* F. L. Warburton, Esq., M.Sc., A.R.C.S., D.I.C., A.Inst.P. (Wool Industries Research Association). (Joint meeting with Huddersfield Textile Society.) Large Hall, College of Technology, **Huddersfield.** 7.30 p.m.

Tuesday, 2nd February 1960

LEEDS JUNIOR BRANCH. *Dyeing Anodised Aluminium.* A. E. Bratt, Esq. (CIBA Clayton Ltd.). The Lecture Theatre, Department of Colour Chemistry and Dyeing, the University, **Leeds 2.** 3.30 p.m.

NORTHERN IRELAND SECTION. *Professional Salesmanship—The Key to Prosperity.* A. B. M. Taylor, Esq. (Irish Linen Guild). (Joint meeting with Textile Institute.) York Street Flax Spinning Co. Ltd., Henry Street, **Belfast.** 7.30 p.m.

Friday, 5th February 1960

LONDON SECTION. *Dyeing and Finishing of 'Courtolon' Nylon in relation to its Yarn Properties.* L. Cotton, Esq., B.A., and J. Wardle, Esq. (Courtaulds Ltd.). Royal Society, Burlington House, **London W.1.** 6 p.m.

Tuesday, 9th February 1960

NORTHERN IRELAND SECTION. *Problems Relating to Permanent Finishes.* Dr. A. Schurch (CIBA Ltd., Basle). Grosvenor Rooms, **Belfast.** 7.30 p.m.

Wednesday, 10th February 1960

MIDLANDS SECTION. *Dyeing and Finishing of Courtolon Yarns, Fabrics and Garments.* J. Wardle, Esq., L. Cotton, Esq., B.Sc. College of Technology, **Leicester.** 7 p.m.

Thursday, 11th February 1960

WEST RIDING SECTION. *Paper Chromatography of Dyestuffs.* J. C. Brown, Esq. (CIBA Clayton Ltd.). Griffin Hotel, Boar Lane, **Leeds 1.** 7.30 p.m.

MANCHESTER JUNIOR BRANCH. *The Photo-chemistry of Aromatic Molecules and Dyestuffs.* Professor G. Porter, M.A., Ph.D., F.R.I.C., Room J/E 11, Chemical Engineering Building (Jackson Street), College of Science and Technology, **Manchester.** 4.30 p.m.

SCOTTISH SECTION *Recent Developments in Wool Dyeing.* W. Beal, Esq., B.Sc. (Geigy Co. Ltd.). (By invitation of the Textile Institute.) Scottish Woollen Technical College, **Galashiels.** 7.30 p.m.

SCOTTISH JUNIOR BRANCH. *Problems relating to Permanent Finishes.* Dr. A. Schurch (CIBA Clayton Ltd.). Technical College, George Street, **Paisley.** 7.30 p.m.

Friday, 12th February 1960

LONDON SECTION. Annual Dinner and Dance. Waldorf Hotel, **London W.C.2.** 7 p.m. for 7.30 p.m.

Tuesday, 16th February 1960

BRADFORD JUNIOR BRANCH. *Developments in the Manufacture and finishing of Terylene–Wool Fabrics.* J. B. Timis, Esq. (I.C.I. Ltd.). Institute of Technology, **Bradford.** 7.15 p.m.

LEEDS JUNIOR BRANCH. *Diffusion Processes in Wool Keratin.* Dr. J. A. Medley (Wool Industries Research Association). The Lecture Theatre, Department of Colour Chemistry and Dyeing, the University, **Leeds 2.** 3.30 p.m.

SCOTTISH SECTION. *The Keratin of Wool.* Professor J. B. Speakman, D.Sc., F.R.I.C., F.T.I. (Joint meeting with the Textile Institute.) The Royal College of Science and Technology, **Glasgow.** 7.30 p.m.

Friday, 19th February 1960

MANCHESTER SECTION. *The Biological Chemistry of Cellulose.* Dr. J. A. Gascoigne (British Rayon Research Association). The Textile Institute, 10 Blackfriars Street, **Manchester.** 7.0 p.m.

Tuesday, 23rd February 1960

SCOTTISH SECTION. *Some observations on the Production of Dyed Yarn for Carpets.* G. B. Angus, Esq., B.Sc., A.R.I.C., A.M.I.I.A., F.S.D.C. (J. Crossley & Sons). St. Enoch Hotel, **Glasgow.** 7.15 p.m.

continued on page iv

FORTHCOMING MEETINGS OF THE SOCIETY — *continued from page* iii

Thursday, 25th February 1960

WEST RIDING SECTION. *New Work on the Dyeing of Nylon with Disperse Dyes.* H. Seaman, Esq., (I.C.I. Ltd.). Victoria Hotel, Bridge Street, **Bradford 1.** 7.30 p.m.

Tuesday, 1st March 1960

LEEDS JUNIOR BRANCH. *Paper Chromatography of Dyestuffs.* J. C. Brown, Esq. (CIBA Clayton Ltd.). The Lecture Theatre, Department of Colour Chemistry and Dyeing, the University, **Leeds 2.** 3.30 p.m.

Friday, 4th March 1960

LONDON SECTION. *Recent Developments in Leather Dyeing.* J. H. Sharphouse, Esq. (Northampton College of Technology). Royal Society, Burlington House, **London W.1.** 6 p.m.

Tuesday, 8th March 1960

NORTHERN IRELAND SECTION. *The Dyeing and Finishing of Fabrics Containing Tricel.* R. J. Mann, Esq., B.Sc., F.S.D.C. (Courtaulds Ltd.). Grosvenor Rooms, **Belfast.** 7.30 p.m.

HUDDERSFIELD SECTION. *Paper Chromatography of Dyestuffs.* J. C. Brown, Esq., B.Sc., A.R.I.C. (CIBA Clayton Ltd.). (Joint meeting with the Huddersfield Section of the Royal Institute of Chemistry.) Silvios Cafe, Westgate, **Huddersfield.** 7.30 p.m.

Thursday, 10th March 1960

MANCHESTER JUNIOR BRANCH. Short Papers by members of the Section. Room J/E 11, Chemical Engineering Building (Jackson Street), College of Science and Technology, **Manchester.** 4.30 p.m.

MIDLANDS SECTION. *The Dyeing of Ribbons.* E. Bridge, Esq. (Joint meeting with the Coventry Textile Society.) Courtaulds Acetate and Synthetic Fibres Laboratory, **Coventry.** 7.30 p.m.

WEST RIDING SECTION. *A comparison of the Dyeing of Acrylics and Worsted Hosiery Yarns.* Dr. J. F. Gaunt (Patons and Baldwins Ltd.). Victoria Hotel, Bridge Street, **Bradford 1.** 7.30 p.m.

Tuesday, 15th March 1960

LEEDS JUNIOR BRANCH. *Management.* Professor Revans (Manchester College of Science and Technology). The Lecture Theatre, Department of Colour Chemistry and Dyeing, the University, **Leeds 2.** 3.30 p.m.

SCOTTISH SECTION. Annual General Meeting 7 p.m. Followed by *Paper Chromatography of Dyestuffs.* J. C. Brown, Esq. (CIBA Clayton Ltd.) St. Enoch Hotel, **Glasgow.** 7.30 p.m.

Wednesday, 16th March 1960

BRADFORD JUNIOR BRANCH. *The Development of a new Shrink-resist Finish from the laboratory to the Mill.* A. N. Davidson, Esq. (Wool Industries Research Association). Institute of Technology, **Bradford.** 7.15 p.m.

Wednesday, 16th March 1960

MIDLANDS SECTION. *Thermal Setting of Tricel.* W. F. Kilby, Esq., B.Sc., A.Inst.P. (Joint meeting with B.A.O.C.) Midland Hotel, **Derby.** 7 p.m.

SCOTTISH JUNIOR BRANCH. Annual General Meeting, 7.0 p.m., followed by a lecture *Paper Chromatography of Dyestuffs.* J. C. Brown, Esq. (CIBA Clayton Ltd.). Technical College, George Street, **Paisley.** 7.30 p.m.

Friday, 18th March 1960

MIDLANDS SECTION. Annual Dinner. George Hotel, **Nottingham.** 7 p.m.

Thursday, 24th March 1960

WEST RIDING SECTION. Annual General Meeting followed by *Problems involved in Piece Dyeing with Vat Dyestuffs.* M. Brauer, Esq. (Badische Anilin & Soda Fabrik A.G.). Victoria Hotel, Bridge Street, **Bradford 1.** 7.30 p.m.

Friday, 25th March 1960

LONDON SECTION. *The Origin of Faults in the Dyeing of Textiles.* N. Jackson, Esq. (Courtaulds Ltd.). George Hotel, **Luton.** 7 p.m.

MANCHESTER SECTION. *New Developments in Textile Printing.* Half Day Symposium. Great Hall, College of Science and Technology, **Manchester.**

Thursday, 7th April 1960

MIDLANDS SECTION. *Recent Developments in Dyeing Wool.* D. B. Evans, Esq. (Joint meeting with the Textile Institute.) Carpet Trades Ltd., Canteen, **Kidderminster.** 7.30 p.m.

Tuesday, 12th April 1960

SCOTTISH SECTION. Ladies Evening. *Interior Design and Decoration.* H. Hellier, Esq. (Glasgow School of Art). St. Enoch Hotel, **Glasgow.** 7.30 p.m.

Wednesday, 13th April 1960

MIDLANDS SECTION. Annual General Meeting. *Colour Photography.* D. P. Ayres, Esq., B.Sc., A.R.P.S. College of Technology, **Leicester.** 7 p.m.

Thursday, 14th April 1960

MANCHESTER JUNIOR BRANCH. Annual General Meeting. Title of paper to be announced later. T. Vickerstaff, Esq., M.Sc., Ph.D., F.S.D.C., Room J/E 11, Chemical Engineering Building (Jackson Street), College of Science and Technology, **Manchester.** 4.30 p.m.

Friday, 15th April 1960

MANCHESTER SECTION. Annual General Meeting. *New Work on the Dyeing of Nylon with Disperse Dyes.* H. Seaman Esq., B.A. (I.C.I. Dyestuffs Division, Blackley). The Textile Institute, 10 Blackfriars Street, **Manchester.** 7.0 p.m.

Tuesday, 19th April 1960

HUDDERSFIELD SECTION. Annual General Meeting. Followed by a lecture *How Colour Photography Works.* D. P. Ayres, Esq., B.Sc. (Ilford Ltd.). Silvios Cafe, Westgate, **Huddersfield.** 7.30 p.m.

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Advance Announcement

The Society of Dyers and Colourists

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The Society of Dyers and Colourists

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NOTICE TO MEMBERS AND SUBSCRIBERS

Readers requiring *general information* regarding the Official Notices, List of Officers of the Society, etc, should consult pages 1–10 of the January 1959 and pages 341–348 of the July 1959 issues of the *Journal*, or write to *The General Secretary*, The Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford 1, Yorkshire (*Telephone* Bradford 25138). *Editorial Communications* should be addressed to *The Editor*, at the same address

Forthcoming Papers

The following papers have been accepted by the Publications Committee, and will appear in future issues of the *Journal*—

LECTURES

The Solubility of Wool Dyes. Its Assessment and Practical Significance — *W. Beal*

Vat Dyeing of Cotton Piece Goods by Pigmentation Routes — *M. R. Fox and J. F. Mawson*

New Ideas in the Application of Phthalocyanine Derivatives to Textiles — *F. Gund*

Some Recent Advances in Textile Printing — *R. J. Hannay*

Aspects of Pigment Dispersion related to Usage — *I. S. Moll*

Some Relations between the Chemical Constitution of Cibacron Dyes and their Dyeing Characteristics — *J. Wegmann*

COMMUNICATIONS

The Pad–Roll Dyeing System. A Summary of Experience — *R. Kern*

Comparison of a Colour Vision Test made from Dyed Wool Patterns with the Ishihara Test — *J. G. Wain*

How Much Research? A Critical Problem in the Manufacture of Textile Dyes — *G. S. J. White*

The Migration of Non-substantive Dyes on Fabrics and its Relation to Saturation Regain and Fibre Surface Structure — *D. Wilson*

The Permanent Creasing of All-wool Fabrics — *M. A. Wolfram and J. B. Speakman*

The Solubilities and Heats of Solution of Disperse Dyes in Water — *D. Patterson and R. P. Sheldon*

I.F.A.T.C.C. 1959 CONGRESS PAPERS

The Application of Reactive and Direct Dyes to Rayon Staple by Continuous Methods — *R. C. Cheetham*

Self-smoothing Cellulosic Fabrics — *J. T. Marsh*

Reactive Dyes for Nylon — *D. F. Scott and T. Vickerstaff*

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THE JOURNAL

OF THE

Society of Dyers and Colourists

Volume 75 Number 12 DECEMBER 1959* Issued Monthly

Proceedings of the Society

The Remazol Linkage

E. Bohnert

One-day Symposium on "Reactive Dyes" held by the Manchester Section at the Manchester College of Science and Technology on 20th March 1959, Mr. J. W. Reidy in the chair

A short introduction to the chemistry of the Remazol reactive dyes is followed by an explanation of their behaviour when applied to cellulosic fibres. An indication is given of the position of Remazol dyes in the general picture of reactive dyes and how they differ from other ranges. Evidence is provided which indicates that a covalent linkage with the cellulose is formed during dyeing. Methods for dyeing fibres other than cellulose are described.

In 1949 Farbwerke Hoechst AG. applied for a patent for a process of fixation of water-soluble organic compounds of the general formula—

$$D\cdot SO_2\cdot CHR\cdot CR^1R^2\cdot O\cdot Z \qquad \text{(i)}$$

on fibrous substrates. On the basis of this application, patents were granted in numerous countries. In addition to compounds of this type, the use of dyes of the following general formula—

$$D\cdot SO_2\cdot CHR\cdot CHR^1\cdot Hal \qquad \text{(ii)}$$

is covered by further patents. In general R, R^1, R^2=H, low-mol. Alk, or Hal; and Z=a polybasic acid group.

In the simplest cases we have compounds of the following types—

$$D\cdot SO_2\cdot CH_2\cdot CH_2\cdot O\cdot SO_3H \qquad \text{(iii)}$$

$$D\cdot SO_2\cdot CH_2\cdot CH_2\cdot Cl \qquad \text{(iv)}$$

If D represents a dye molecule which contains one or more solubilising groups, we have the general formula for the Remazol dyes [1].

The purpose of this paper is to show how this range of dyes and their reactive groups behave under the conditions usually existing in dyeing and printing processes, pointing out how they differ from other types of reactive dyes, and to what extent their behaviour fits into the general principles of coloration with reactive dyes.

REACTIONS OF REMAZOL DYES UNDER ALKALINE CONDITIONS

In organic compounds the sulphonyl group induces polarisation of an aliphatic chain to which it is linked. The carbon atom in the α position to the sulphonyl group has an electron-restraining effect, thus being of a negative character, whilst the carbon atom in the β position becomes of a positive character. We can symbolise this polarisation by writing the formula of the Remazol dyes—

$$\underset{}{D\cdot SO_2\cdot \overset{\alpha}{\underset{}{CH_2}}\cdot \overset{\beta}{\underset{}{CH_2}}\cdot O\cdot SO_3Na} \qquad \text{(v)}$$

The electrons belonging to the hydrogen atoms linked to the α carbon are nearer the carbon atom than the hydrogen atoms. On the other hand, the electrons in the neighbourhood of the β carbon are not as strongly linked to this atom. At the α carbon there is a tendency to liberate a proton, and the $O\cdot SO_3Na$ group linked to the β carbon is likely to separate as an anion. In alkaline medium these tendencies are realised in the following reaction, which leads to the formation of the vinyl sulphone—

$$D\cdot SO_2\cdot CH_2\cdot CH_2\cdot O\cdot SO_3Na + NaOH \rightarrow D\cdot SO_2\cdot CH{:}CH_2 + Na_2SO_4 + H_2O \qquad \text{(vi)}$$

The formation of the vinyl sulphone is analogous to the formation of $\alpha\beta$-unsaturated carbonyl compounds from β-halogenocarbonyl compounds under the influence of alkali. As the α carbon is more strongly affected by the sulphonyl than by the carbonyl group, reaction (vi) occurs more rapidly and under milder conditions than with the corresponding carbonyl compounds.

The treatment of sulphuric acid esters of hydroxyethyl sulphones with alkali is a method for the preparation of vinyl sulphones, and it is possible to isolate the vinylsulphonyl dye formed by the treatment of a Remazol dye with alkali.

Reaction (vi) takes place almost immediately on addition of an alkali to an aqueous solution of a Remazol dye. The course of the reaction can be followed very easily by measuring the pH of a concentrated dye solution during the addition of alkali. It is advantageous to use a strong alkali

* Published January 1960

such as caustic soda for the test, as it causes a considerable rise in pH if it is not neutralised immediately after the addition. If we add the alkali drop by drop from a burette at room temperature we observe only an increase of the pH to 10–10·5 as long as the total quantity of alkali does not exceed that corresponding to the above equation. As soon as the added alkali is equivalent to the amount of dye in solution, any further addition causes a rapid increase of pH.

This experiment does not give final proof that the reaction caused by the alkali is the one shown in (vi). The neutralisation of the alkali could also be produced by the following reaction—

$$\begin{aligned} &D\cdot SO_2\cdot CH_2\cdot CH_2\cdot O\cdot SO_3Na + NaOH \\ &\rightarrow D\cdot SO_2\cdot CH_2\cdot CH_2OH + Na_2SO_4 \end{aligned} \qquad \text{(vii)}$$

Which of the two reactions actually takes place can be established by a simple dyeing test.

The hydroxyethyl sulphone which would be formed in reaction (vii) does not possess any reactivity. A dye containing this group thus shows no affinity for cellulosic fibres if, as with the Remazol dyes, the dye molecule itself has no affinity for these fibres. However, Remazol dyes which have been treated with the equivalent amount of alkali do not lose their activity. Their solutions dye cellulosic fibres to the same depth of colour as the dyes which have not been pretreated with alkali, provided that the total amount of alkali used is the same in both cases.

Thus it has been shown that the primary reaction of the Remazol dyes leads to the formation of vinyl sulphones, and hence the vinylsulphonyl group can be regarded as the true reactive group of this class of dyes. Two important attributes of these dyes can be explained in the light of this information.

The dyes contain in their reactive group (before treatment with alkali) a solubilising radical which accounts for their high solubility. In neutral aqueous solution the Remazol dyes do not undergo any chemical reaction, and they can consequently be boiled without running the risk of hydrolysis. Neutral solutions are stable and can be stored at room temperature for a long time.

The vinylsulphonyl group, as a result of the mobility of the π electrons in the double bond, shows particularly strong polarisation caused by the sulphonyl group—

$$D\cdot SO_2\cdot \overset{\delta^-}{C}H=\overset{\delta^+}{C}H_2 \qquad \text{(viii)}$$

This activated double bond is able to undergo addition reactions, e.g. with water and alcohols, including, of course, cellulose—

$$D\cdot SO_2\cdot CH{:}CH_2 + R\cdot OH \xrightarrow{OH^-} D\cdot SO_2\cdot CH_2\cdot CH_2\cdot O\cdot R \qquad \text{(ix)}$$

With both alcohols and cellulose, ethers are formed, and with water the hydroxyethyl sulphone is produced. In the dyeing of cellulosic fibres the addition reaction with the cellulose molecule is always accompanied by the addition reaction with water and, consequently, the dyeing conditions must be selected in such a way that the reaction with the fibre is favoured.

In contrast to the chlorotriazinyl dyes, which react with both fibre and water by *substitution* reactions, the liberated acid being neutralised by the alkali present in the liquor, the vinyl sulphone dyes react by an *addition* reaction catalysed by alkali. In dyeing with Remazol dyes alkali is consumed only during the formation of the vinyl sulphone from the ester, not during the actual reaction with the fibre. The secondary reaction with water, which always accompanies the dyeing process, is typical of all types of reactive dyes, and takes place to the same extent with the Remazols as with the other types.

REACTIVITY OF THE VINYLSULPHONYL DYES

It seems possible to deduce the reactivity of a range of reactive dyes from the recommended alkali and dyeing temperatures. Since with the Remazol dyes in long-liquor dyeing a temperature of 60°C. and soda ash or trisodium phosphate are recommended, it can be concluded that their reactivity lies between those of the di- and the mono-chlorotriazinyl dyes. This conclusion is correct, and is confirmed by the following experiments and considerations.

The reactivity of the vinylsulphonyl group increases with both temperature and pH, and is influenced also by the distribution of energy throughout the dye molecule. Theoretically the Remazol dyes could be applied to cotton at 20–30°C. The reason why this temperature is not generally recommended is that some members of the present range will give a good yield on cotton at this low temperature in a commercially acceptable dyeing time only if the pH is adjusted to a definite value with caustic soda. If trisodium phosphate is used as the alkali, the dyeing times at the pH values attained are far too long to be considered in practice. This means that the vinylsulphonyl group possesses at 20–30°C. a distinct but, on the average, lower activity than the dichlorotriazinyl group, which at these temperatures is able to react with cellulose under pH conditions which can easily be obtained with soda ash.

Cotton can be dyed with Remazol dyes in long liquor ratios also at temperatures above 60°C., with a corresponding decrease in the alkalinity. At the boil, for example, the alkalinity obtained with soap is high enough to induce the desired reaction.

The temperature of 60°C. recommended at present is obviously a compromise. It was chosen because all members of the present range yield satisfactory and reproducible dyeings at this temperature, even when used in mixtures. The use of soda ash or trisodium phosphate to adjust the pH ensures that there is only a slight difference in its value should the correct amount not be taken. These pH differences and a slight variation in temperatures have hardly any influence on the results obtained under these general conditions, and this process offers, at least for the present, the best reproducibility of results.

REACTION OF THE VINYLSULPHONYL DYES WITH CELLULOSE

The addition reaction between the vinylsulphonyl dyes formed in alkaline solution and cellulose is

catalysed by hydroxyl ions, and the dye becomes linked with the fibre by an ether linkage. The speed of the reaction should be greater the higher the temperature and the higher the pH of the liquor. Consequently it would be expected to be advantageous to increase the pH to as high a value as possible at the place where the reaction is to take place, i.e. within the fibre itself. This, however, is true only to a limited extent. Particularly at higher temperatures the reaction with the fibre is not sufficiently favoured if the pH is higher than the optimum value, as the reaction with water attains a similar speed. Furthermore, under extreme conditions the link between the dye and the cellulose can be split—

$$D\text{-}SO_2\text{-}CH_2\text{-}CH_2\text{-}O\text{-}Cell + H_2O \xrightarrow{OH^-} Cellulose + D\text{-}SO_2\text{-}CH_2\text{-}CH_2OH \quad (x)$$

There is a definite pH value for each dye at which its reaction with cellulose at a given temperature is particularly favourable.

It must therefore be our main effort to adjust the pH within the fibre to this optimum value and to take care that at the same time the pH of the liquor remains low, in order to retard as much as possible the simultaneous addition reaction with water. To achieve this we can advantageously make use of the ability of cellulosic fibres to absorb alkali, the importance of which in the application of reactive dyes has already been discussed by Vickerstaff[2]. It appears to be decisive for dyeing in long liquors, because it enables the reaction in the interior of the fibre to proceed much faster with the cellulose than with the water in the dyebath. In this respect there is complete similarity in behaviour between the Remazol dyes and the chlorotriazinyl ranges.

The Remazol dyes require, as do the other reactive dyes, the addition of salt to the dye liquor. At least part of the effect of the salt is due to increase in the difference in pH between the liquor and the interior of the fibre[3], and therefore large amounts of salt would appear to be desirable. In fact, with some dyes, there is a considerable increase in yield if salt concentrations considerably greater than the normal 50 g./litre are used, but this makes the dyeing process uneconomic at liquor ratios as long as 20–30:1.

Since dyes of the hydroxyethyl sulphone type—

$$D\text{-}SO_2\text{-}CH_2\text{-}CH_2OH \quad (xi)$$

are formed as by-products on the addition of water to the vinyl sulphone dyes, they are always produced during dyeing and printing with Remazol dyes; but as they do not have any affinity for cellulosic fibres, and are readily soluble in water, they can be removed from the fibre by a simple scouring process. When prints obtained with Remazol dyes are washed after steaming, a normal open-width scouring range is sufficient to remove the unfixed dye from the fibre. The wet fabric can be stored before drying without running any risk that bleeding will take place.

PROPERTIES OF REMAZOL DYEINGS ON CELLULOSE

The extreme conditions necessary to split the dye–fibre ether linkage are produced if strong alkali acts on the dyeing at a high temperature. At the boil the alkalinity of soda ash may in some cases be sufficient to rupture the linkage. This is the reason why, with some Remazol dyes on cotton, the ISO test for fastness to washing at 95°C. causes a slight loss in depth of colour and traces of bleeding on to white fabric. Up to 75°C. there is no danger of colour loss nor of bleeding with any of the Remazol dyes, even in the presence of soda ash. In a wash-fastness test at the boil, in which synthetic detergents of neutral reaction are used, none of the Remazol dyes shows colour loss or bleeding, even if the test is repeated several times. The dyes can therefore be used for any article which is not likely to be washed severely during its normal usage. For articles which are normally subjected to severe washing conditions reactive dyes cannot compete, in my view, with suitable vat, leuco vat, and azoic dyes.

The other wet-fastness properties of interest to the user are very good. Some of the Remazol dyes even possess good fastness to chlorine—

Remazol Yellow RT
Remazol Red 3B
Remazol Red Violet R
Remazol Brilliant Violet 5R
Remazol Brilliant Blue R.

With the exception of Remazol Brilliant Blue R the fastness to burnt-gas fumes (oxides of nitrogen) is good.

The stability of the Remazol linkage with the fibre is not strong enough in alkaline medium to withstand extreme conditions, but this is compensated for by its stability under acid conditions, which can be of importance during storage and use in industrial areas, where quite often the air contains acid fumes such as sulphur dioxide, and the fastness to cross-dyeing also depends on this acid stability.

The light fastnesses range from good to excellent, depending on the dye, the depth of colour, and the material. Remazol dyeings have good dischargeability, partly because of the weakness of the linkage under strongly alkaline conditions. In addition to the destruction of the dye molecule by the reducing agent, the link between the dye molecule and the fibre is split, and this reduced dye can also be washed off. Thus, in a discharge on a dyeing of Remazol Red B in which a small amount of alkali is used, a distinct red is developed on diazotising and coupling; but in a discharge produced with higher quantities of alkali, no residual base is linked to the fibre which could be recoupled.

EVIDENCE OF CHEMICAL LINK WITH FIBRE

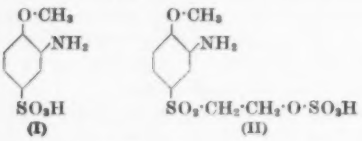
There is some indirect evidence about the Remazol linkage to cellulose. If a Remazol dyeing of an azo dye is destroyed by reducing the azo group, and after thorough scouring and soaping the colourless fibre is diazotised and then treated with a solution of a coupling component, the fibre can be redyed. If the coupling component is the same as in the original dye, which had its reactive group in the base, then the original dyeing is reformed—

$$\text{Cell·O·CH}_2\text{·CH}_2\text{·SO}_2\text{·Base·N:N·Coupl·SO}_3\text{Na} \xrightarrow{\text{Reduce}} \text{Cell·O·CH}_2\text{·CH}_2\text{·SO}_2\text{·Base·NH}_2 + \text{H}_2\text{N·Coupl·SO}_3\text{Na}$$

$$\text{Cell·O·CH}_2\text{·CH}_2\text{·SO}_2\text{·Base·N}^+\text{:N}\}\text{Cl} + \text{Coupl·SO}_3\text{Na} \longrightarrow \text{Cell·O·CH}_2\text{·CH}_2\text{·SO}_2\text{·Base·N:N·Coupl·SO}_3\text{Na}$$

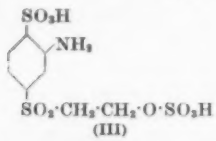
This proves that the part of the dye molecule which contains the reactive group has not been removed from the fibre.

The following test shows that it is possible first to apply a base which contains the reactive group, and then to diazotise and develop it on the fibre. Three bases (I–III) were printed in an alginate thickening together with sodium bicarbonate on cotton. After drying, the prints were steamed.



(I)

(II)



(III)

It is not important whether the steamed prints are diazotised immediately and developed with 1-naphthol-5-sulphonic acid or whether they are first thoroughly washed and soaped before this process. Only with II and III was a coloured fibre obtained, which is fast to washing. The difference in colour obtained with III (orange) compared with II (red) is due to the replacement of $O{\cdot}CH_3$ by SO_3H.

Remazol dyeings are resistant to neutral organic solvents. Even dimethylformamide, a solvent which causes bleeding with most other classes of dyes, cannot dissolve Remazol dyes, which are linked to the fibre.

Wegmann[4] has shown that the solubility of cellulose in cuprammonium is affected only if the dye used contains at least two reactive groups and is thus able to cross-link the cellulose molecules, and this is observed with Remazol dyes. Thus cotton dyed with Remazol Brilliant Blue R, which contains one reactive group, dissolves readily in cuprammonium, whilst Remazol Black B, which contains two reactive groups, makes cotton insoluble in this medium.

In combination with the fact that a Remazol dye applied to cotton by padding can be removed from the fibre if it is not fixed with alkali, we can draw the conclusion from these tests that dyeings and prints made with Remazol dyes owe their properties to a chemical link with the fibre.

DYEINGS ON FIBRES OTHER THAN CELLULOSE

At pH < 7 the Remazol dyes show remarkably high stability. Even in N. sulphuric acid solution at the boil they are transformed to the hydroxyethyl sulphones only very slowly, i.e. after hours of boiling. There seems to be no formation of the vinyl sulphones in acid solution.

If wool is present in an acid solution of a Remazol dye, the amino groups in the fibre can react with the dye. As the reactivity of the Remazol dye is the greater the higher the pH, dyeing of wool in a neutral or only slightly acid medium would favour the reaction between dye and fibre. Because of the insufficient exhaustion under these conditions the following process is recommended for the dyeing of wool with the present range of Remazol dyes. Add to the liquor—

—	Dye
5%	Glauber's salt (anhydrous)
4%	Sulphuric acid (96%).

Enter the goods at 40°C., raise the temperature to 60°C. within 30 min. and keep at this temperature for 10 min. Then raise to the boil in 20 min. and continue boiling for 60 min. The addition of Remol GE (a levelling agent) is advantageous with Remazols Yellow RT, Red Violet R, and Black B.

In this dyeing method only part of the dye on the fibre is chemically linked with the wool. The remainder is fixed like a normal wool dye. The dyeings have good levelness and possess good wet fastness. The wet fastness is between that of acid dyes of the Supramin (FBy) range and that of milling dyes. The light fastnesses are 6 or better, except for dyeings with Remazol Red B.

Polyamide fibres can be dyed by the same method.

Acrilan acrylic fibre also can be dyed with Remazol dyes from a strongly acid dyebath. Remazol Black B can be recommended for the production of a deep black with good fastness properties. The other dyes are less fast to light and therefore not generally suitable for this fibre.

The process recommended for the dyeing of silk was established on a purely empirical basis. It is most likely that under alkaline conditions a much greater proportion of the dye is able to react covalently with the fibre than under acid conditions. The process is as follows—

Enter the goods into the cold dyebath containing 10 g. Glauber's salt (anhydrous) per litre, raise the temperature in 30 min. to 60°C., adding during this period two portions of Glauber's salt (each 20 g./litre). At 60°C. add twice, at intervals of 10 min., 1 g. soda ash per litre, and maintain at 60°C. for a further 45 min. Then rinse and treat at 80–85°C. with (per litre)—

5 g. Glauber's salt (anhydrous)
1 g. Soda ash
1 g. Hostapon T

for a period of 10 min. Then rinse and treat with dilute acetic acid.

Although at present the main field of application of the Remazol dyes will be the dyeing and printing of cellulosic fibres, they will help to solve problems that exist in dyeing the other fibres mentioned.

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(*MS. received 3rd June 1959*)

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[4] Wegmann, J., *ibid.*, **39**, 1006 (1958).

Discussion

Dr. T. VICKERSTAFF: Can Dr. Bohnert say whether he considers that the difference between the internal and external pH of cellulose fibres is the only factor producing a greater rate of reaction with the fibre, or whether he considers that the hydroxyl groups on cellulose are more reactive than aqueous hydroxyl groups, as suggested by Mr. A. S. Fern?

Dr. BOHNERT: Investigations [3] that have been made into the kinetics of dyeing with Remazol dyes have shown that the activation energy of the reaction of the Remazol dyes with the cellulose is distinctly lower than that of the reaction with water. This proves that the reaction of the vinylsulphonyl group with the OH groups of the cellulose is more favoured than with the OH groups of the water. This, in my opinion, is the reason why in pad dyeing and printing more than 50% of the dye used is linked with the cellulose. The difference between the internal and external pH has its main importance in long-liquor dyeing. With its assistance we can establish conditions which cause a slow reaction with the water in the dyebath and, because of the higher pH within the fibre, a faster reaction with both the fibre and the water in the fibre pores. The lower activation energy of the reaction with the cellulose here again favours the reaction with the fibre rather than the hydrolysis reaction (within the fibre pores). If there were no difference between the internal and external pH we could hardly expect that the yield in long-liquor dyeing would be good enough to make this method of application of practical value.

Mr. P. JAEGER: Could the vinyl sulphone dyes be produced and handled alone, or are they stable only as an intermediate in the dyeing process?

Dr. BOHNERT: There is no particular difficulty in producing and handling vinyl sulphone dyes. The dyeing results are the same as those obtained with the Remazol dyes.

Dr. L. VALENTINE: Dr. Bohnert has shown that the Remazol dyes normally react under alkaline conditions, and are relatively stable under acid conditions. They do, however, give fast dyeings on Acrilan under acid conditions. What is the mechanism of their action in this case? Are they still strictly reactive dyes?

Dr. BOHNERT: The mechanism of the dyeing of Acrilan with Remazol dyes has not yet been investigated. In all probability only part of the dye will react with the basic groups of the Acrilan under the strongly acid dyeing conditions, the rest being fixed in a similar manner to an acid dye.

Dr. J. R. HOLKER: Has the author ever observed any polymerisation through the vinyl groups, leading to the formation of high-molecular-weight polymeric dyes during the application of Remazol dyes? This could explain the dyeing of Acrilan, without requiring any reactive centres.

Dr. BOHNERT: So far no polymerisation has been detected during the application of Remazol dyes.

Tests for Colour Vision

F. JORDINSON and T. MINSHALL

Meetings of the Huddersfield Section held jointly with the Huddersfield Section of the Royal Institute of Chemistry at Silvio's Café, Huddersfield, on 21st January 1958, Dr. E. Tittensor in the chair; and of the Bradford Junior Branch held at the Bradford Institute of Technology, on 19th October 1959, Mr. R. S. Harding in the chair

The various types and degrees of defective colour vision are discussed, leading to many different kinds of tests, which may be valuable and successful for certain purposes but less so for others. Special tests are required for dyers and colour blenders, where even a slight variation from normal colour vision is quite an important matter. The Wain test, which has been developed on the basis of metameric matches, is claimed to be extremely sensitive for this purpose.

In a previous paper [1] it has been pointed out that it is impossible to define normal colour vision, and that observers commonly referred to in the literature as "normal observers" show slight variations in colour sensitivity. This is illustrated by the disagreement shown by "normal observers" when using a colorimeter to make a series of colour matches. By subjecting these results to statistical analysis it is evident that this difference is partly due to experimental error, as they are grouped around an average figure.

However, in other cases, even with people having apparently normal colour vision, the average figure differs from the previous mean by an amount not explainable by experimental error, and the variations within a random group of individuals are quite considerable. It is probable that these deviations between observers may be explained chiefly on the basis of variations in the amount of yellow pigment present in the foveal region of the retina. A similar effect occurs in late adult life due to the crystalline lens of the eye becoming tinged with a yellow pigment. These may be regarded as physical variations between individuals giving rise to variations in colour vision which can be corrected by the use of filters. On the other hand, as is well known, there is no means of correcting variations in colour vision which are due

to defects in the physiological mechanism of vision. The term "defective colour vision" is usually restricted to the latter variations. The presence of these pigmentation variations is one of the factors which gives rise to the difficulties encountered in devising suitable tests for defective colour vision.

Tests have been made on a large number of people having so called "normal" colour vision, and the mean of their results has been taken as indicating the average or standard observer. Originally these tests were carried out with a trichromatic colorimeter using a 2° field in order to correspond to foveal vision, i.e. the rod-free central area of the retina. Recently, however, in work by Stiles [2] and others [3] on the redetermination of the standard observer, a 10° field is preferred, as it is now recognised that the peripheral retina is by no means colour-blind.

Persons whose colour vision falls plainly outside these limits are considered to have defective colour vision, and for practical purposes the different kinds of congenital colour deficiencies may be classified as follows—

A. TOTAL COLOUR-BLINDNESS (MONOCHROMACY—This is a very rare group, who can distinguish only between black and white. The defect is usually associated with other optical defects such as low visual acuity, photophobia, and "congenital" nystagmus. Another interesting characteristic of monochromacy is that maximum photopic (light-adapted) brightness occurs in the region which in a normal person coincides with the scotopic peak, viz. 500 mμ.

B. DICHROMACY (only variation between two colours—

(1) Protanopy (red blindness)
(2) Deuteranopy (green blindness)
(3) Tritanopy (blue blindness).

Often protanopes and deuteranopes are grouped together as red–green colour-blinds, or sometimes as anopes, as in practice they give rise to similar colour-perception defects. Tritanopia is very rare, but much scientific interest has been focused upon it in recent years.

C. ANOMALOUS TRICHROMACY—Such people can detect many colours, but have a reduced sensitivity towards a definite colour—

(1) Protanomalous or red-weak
(2) Deuteranomalous or green-weak
(3) Tritanomalous or blue-weak.

Protanomalous and deuteranomalous persons are generally referred to as "colour-weak". Tritanomalous people are extremely rare. Groups B and C together comprise 8% of all men and 0·5% of women. It should be pointed out that colour discrimination can be developed in some people, particularly if training is commenced at an early age. In the dyeing industry such training can improve colour discrimination to a high level, even though it may be associated with some degree of colour deficiency. The above classification refers both to additive and to subtractive colour matching. Dichromats are so called because they match using two stimuli only, compared with normal observers who have trichromatic vision, i.e. they use three primaries to produce sensations of colour. Anomalous trichromats also require three primaries when producing certain colour sensations, but they do so in abnormal proportions compared with the standard observer.

Using a tristimulus colorimeter it is possible (by matching a coloured light of known wavelength with mixed lights of other quality) to ascertain the degree of abnormality in the colour vision of a dichromat or an anomalous trichromat. Such instruments, however, are expensive and require a certain amount of scientific training for their operation, so that in practice colorimetric methods are left to the research worker. For practical testing for industry and for the Armed Forces, simplified tests are naturally preferred which will give a general picture of the extent of the defective colour vision. Originally these simplified tests were designed merely to ascertain whether a person suffered from red–green blindness. Since in most occupations it does not matter whether a person is a protanope or a deuteranope, no attempt was made to differentiate between them. With increased refinement in methods of testing and as a result of greater world-wide interest in the whole problem of defective colour vision, tests are now available which claim to be able to distinguish between red-blindness and green-blindness, and indeed blue-blindness also. Considerable success has attended these efforts, but the problems of detecting defective colour vision from a physiological aspect are formidable, and the interpretation of the tests is not easy.

For example, it is obvious that there are variations in the nature and degree of the types of dichromatic and anomalous trichromatic vision which have been previously listed. Again, although most forms of colour-blindness are inherited, others may develop with increasing age or be acquired, e.g. as a result of illness. Diseases of the optic nerve or of the retina often involve loss of colour vision, although usually this is a secondary feature compared with loss of form vision. A condition known as toxic amblyopia, due to the effect of certain poisons on the ganglion cells of the retina, is associated with defective colour vision. The symptoms are a gradual impairing of visual acuity—actually central scotoma—along with some loss of colour perception, also in the central area. Medical opinion attributes this condition to the result of heavy smoking (especially of heavy pipe tobaccos) or alcohol, or a combination of both. If the cause is removed, there is usually a gradual improvement, and vision (form and colour) returns to normal.

A colour (light or pigment) can often be named correctly if present as large areas or as bright colours. This relationship between luminosity (brightness) and colour vision is extremely important, and there is considerable support for the theory that information about brightness and colour is carried from the retina to the external

geniculate body by fibres represented by Granit as "dominators" and "modulators". The dominators merely inform the centres in terms of brightness and are much more numerous (95%) than the modulators (5%). Their comparative abundance readily explains why a stimulus becomes less and less coloured as its size diminishes. On the other hand, the modulators are considered to be responsible for colour discrimination. Actually seven modulators have been found, but they fall roughly into three groups in the red, green, and blue parts of the spectrum, which is in general agreement with the trichromatic theory of colour vision.

An interesting difference between deuteranopic (also deuteranomalous) vision and protanopic (including protanomalous) vision results from a study of luminosity data. The latter types are *less* sensitive to red, whereas the former show approximately the *same* relative sensitivity to red and green as those having normal colour vision. Ellis [4] has recently pointed out that for cone receptors the comparative luminosity of radiations of red light of 630 mμ. and above in the case of normal observers is six times that of some defective observers, who thus quite easily confuse a full red with black. Tests are being developed which attempt to make use of these facts for detecting the various degrees of red-blindness.

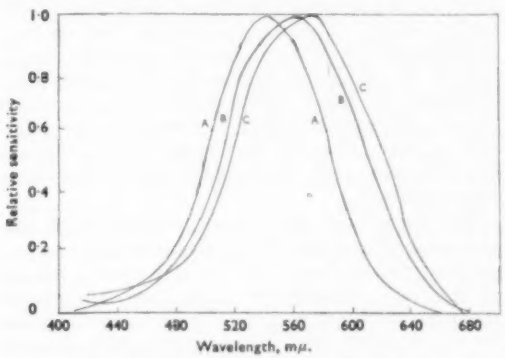


FIG. 1—Spectral Curves of Protanopic (A) and Deuteranopic (C) Vision compared with the Normal Sensitivity Curve (B)

Colour Vision Tests

On account of the world-wide interest in this matter a very large number of tests have been devised, and precise classification is becoming increasingly difficult. Those which will be discussed in this paper may be classified as follows—

(1) Confusion-chart tests or pseudoisochromatic charts, i.e. false perception of similarly coloured plates

(2) Lantern tests, in which the observer is asked to name the colour of light exposed to view

(3) Matching tests, which have developed from the early Holmgren test, which used matching skeins of dyed wool.

CONFUSION-CHART TESTS

The Ishihara Test

This test [1] was commended by the Physical Society Colour Group [5], but has been somewhat severely criticised in recent years.

Hardy, Rand, and Rittler [6] state that it fails to give an accurate assessment of the nature or degree of a person's colour deficiency, even when administered by a careful and experienced tester. Deuteranomalous persons give results which depend on the nature of the illuminant used. These authors conclude that results obtained by using the Ishihara test should be discounted unless supplemented or verified by other tests. This is in line with certain modern American ideas of using a battery of different types of colour vision tests to obtain full and reliable information. It is argued that the Ishihara test should be used merely as a gross test of defective red–green colour vision, and that for this purpose only a few of the Ishihara plates are really required.

Pickford [7] arrives at a similar conclusion in a comprehensive analysis of the 8th edition (Japanese) of the Ishihara test. He finds that many of the plates are unreliable for sorting out normal observers from major defectives. Other plates err in having too many alternative interpretations, in particular many of those having double numbers. He recommends a shortened form— consisting of No. 10, 11, 14, 15, 18, and 23 (best of the two-number plates)— which sorts out red–green dichromats and protanomalous observers. Even when using this test, no type of minor defective can be effectively distinguished. Deuteranomalous observers give the largest variety of alternative readings and often see both the "normal" and the "defective" reading for some plates.

Whilst it may be admitted that a shortened version of this (and of other pseudoisochromatic tests) gives better results in separating colour defectives from those having normal colour vision, it is well to remember that the Ishihara test is also used for rapid testing of large bodies of men in the Armed Forces. Here the large number of plates reduces the possibility of learning the answers by heart and so defeating the purpose of the test.

The ingenious plates No. 22–25 (7–9th editions), which claim to be able to differentiate between red-blindness and green-blindness, attempt to exploit the fact that red-defectives cannot discern reds and blue–greens, whereas green-defectives find difficulty with greens and purples. Taking No. 23 as an example, a normal observer sees the number 42 on a background of varying tones of grey, the 4 being in red and the 2 in purple. A protanope cannot see the 4 against the grey background on account of his low sensitivity to red wavelengths; he therefore reads only the 2. Similarly, a deuteranope fails to see the purple 2, which is a mixture of red and blue so arranged as to produce a match for a spectral colour at his neutral point. He reads the 4, but the 2 appears grey against the grey background, and so cannot be seen. Thus the colours of both figures correspond to the neutral point (on the purple tones) of the appropriate type of dichromat.

These plates, however, work out rather disappointingly in practice, and Pickford [7] states that, although normal observers seldom make any errors with them, they are unreliable for all types of

major defectives. In a test carried out recently by the present authors, the subject read only the red figure 2 in Plate 22 (indicating green-blindness) and only the purple figure 2 in Plate 23 (denoting red-blindness).

In criticising the Ishihara test, it is only fair to point out that the 9th edition was reprinted in London during the war using inks which had not necessarily the same reflectance properties as the corresponding 8th (Japanese) edition. Also the 10th edition, printed in Japan in 1951, has been completely revised and now has 38 plates in which the colouring is clearer than in the 9th edition, thus making the numerals and winding lines stand out more clearly.

The Stilling Test

The first edition of these well-known pseudo-isochromatic plates was brought out in 1876 by the German anatomist B. Stilling, and there have been many subsequent editions. The general principle on which they are based is very similar to the Ishihara and so is the method of using them. The early editions were not very successful, as the coloured numerals made up of little dots were much brighter than the coloured background on which they were superimposed. Many colour-defectives were quick to take advantage of this difference in brightness in order to ascertain the numbers. Later editions corrected this fault, and seventeen editions had been published by 1926.

A feature of these later editions was the special attention which was paid to tritanopia. For example, in the 17th edition some blue–green and blue–yellow plates were included. Pickford [7] reports an investigation into the use of these plates and is critical of the blue–yellow plates, as he finds that they are easily read by extreme tritanopes, who see the yellowish figures as almost white, which is clearly different from the blue. The blue–green plates do cause much difficulty to tritanopes, but this applies also to other types of colour-defectives.

Hertel [8] developed a series of tests based largely on Stilling's principles, which formed the 20th edition of the Stilling–Hertel plates. The present (21st) edition was published in 1952, and it contains an extremely interesting series of plates which embody several testing procedures. There are several pseudoisochromatic plates, some of which appear to have been incorporated into the American Optical Company test [9], also some pseudo-nonisochromatic plates described as "Vexier" (puzzle) plates. In most of these plates the red–green colour-defective reads a different number or figure from the normal observer. Four of this series (No. 21–24) are also stated to be for the special recognition of tritanopia, but the blue–green colours of Plate 21 and the pink–scarlet colours of Plate 22 cause difficulty to some red–green defectives. For specific detection of gross tritanopia there remain No. 23 and 24, also No. K4 and K6.

The K series of plates (K1–K7) is based on increasing colour contrast and is of entirely different construction from the plates previously mentioned. Against a vivid background of red, green, yellow, and blue is placed a circle or figure which the person having normal colour vision correctly reads as grey. Colour-defectives, however, see them as pink (red), green, blue, or yellow depending on the nature of their colour deficiency.

In the remaining four plates (F1–F4) the above effects are reversed, as they depend on diminishing colour contrast brought about by placing a sheet of tracing paper in front of the saturated ground colours, on which are shown grey–black letters or figures. These grey shapes to persons of normal colour vision change over to the complementary colour (red, green, blue, or yellow) of the background. On the other hand, the grey shapes can hardly be seen at all by colour-defectives on account of their lower degree of sensitivity to the ground colours. These four "Florcontrast" plates are very sensitive and readily detect anomalous trichromats. They should be read at a distance of 30 cm. using reading glasses, but the other plates require distance spectacles and are offered at a distance of 1 metre.

The American Optical Company Pseudoisochromatic Plates [9]

These plates are understood to have been formed (1940) by reproducing plates from both Stilling and Ishihara tests. They are so arranged that a person with normal colour vision can recognise the figures against the irregular background by means of a difference in hue. Dichromats and anomalous trichromats have difficulty in perceiving the numbers (or wavy line), as they have to rely solely on hue difference and cannot make use of brightness discrimination.

The tints used have been selected with the assistance of a colour-blind painter so as to correspond to the confusion colour of a person who is colour-blind. Altogether there are 46 plates, many of which are very similar in the hues chosen for the numerals and background. It is not surprising that a Revised Selection of the American Optical Company Plates (1945) cut down the number to 18 from the original 46. Using these carefully selected revised plates, it is claimed that an observer who fails on four or more charts can be classified as definitely colour-defective. As they are now being widely used in the U.S.A., they constitute a very important up-to-date series of confusion charts, which are proving valuable for sorting out colour-defectives. Persons with mild degrees of defective colour vision can sometimes name correctly some numbers after a certain amount of hesitation, compared with complete inability to do this in more severe cases of colour blindness. It is not claimed that the revised test can reliably differentiate between dichromats and anomalous trichromats, but it is proving useful for sorting out people having some degree of colour weakness.

The American Optical Company's plates have been superseded (1955) by an entirely new set based on confusion with grey for the different types of observer.

LANTERN TESTS

The Giles–Archer Colour Perception Unit [10]

This is a modern example which has the advantage of being portable and which can be plugged into a standard lamp socket. A 15-watt lamp shines through a rotatable disc which carries six gelatin filters— (1) dark red (D.R.), (2) standard red (R), (3) standard yellow (Y), (4) signal green (S.G.), (5) green (G), and (6) clear aperture.

The lamp house is fitted with a slide having three apertures as follows— (*a*) 5 mm. aperture, (*b*) 0·5 mm. aperture, (*c*) 0·5 mm. aperture with neutral filter. It will be appreciated that, when using apertures (*b*) or (*c*), the difficulty of naming the coloured discs is increased, and colour-defectives can be more easily detected.

The test is quite simple to carry out, and merely consists in showing the complete sequence of discs through the large aperture, asking the candidate to name the colours, at a distance from the lamp of at least 6 metres. The test is repeated using aperture (*b*) and finally with aperture (*c*). For true results the subject should first be dark-adapted, by leaving him in the dark for 15 min. before examination. Severe cases of red or green blindness cannot differentiate between the red and green discs or cannot even see them at all, especially when the smaller apertures are used.

The compilers claim that it is a practical test which simulates coloured lights under approximately working conditions, and that it is particularly suitable for the requirements of the Admiralty and other services who use a combined testing technique. This comprises a confusion test—usually the Ishihara—along with a lantern test. The Ishihara test, which of course does not involve the naming of colours, is given first in daylight; this is followed by a period of 15 min. dark adaptation, then the lantern test is given as just described. Such a test using coloured lights has obvious advantages for testing persons who are expected to be able to differentiate and to name the colours of signal lights.

The makers of the test also offer an aviation model, which is designed to provide the Royal Air Force with a colour vision test which incorporates the standard colours of the International Committee for Aerial Navigation (I.C.A.N.). It differs slightly from the regular model just described, as the smallest aperture is 1 mm. instead of 0·5 mm., and frosted screens are used to give the effect of poor visibility. Two additional filters are incorporated, viz. standard yellow and standard green. The eight discs are, therefore— (1) dark red (D.R.), (2) yellow (Y), (3) standard red (S.R.), (4) standard yellow (S.Y.), (5) standard green (S.G.), (6) blue-green (signal green) (B.G.), (7) light green (L.G.), and (8) clear aperture.

The method of carrying out the test is similar to that which is used for the regular model, but there are obvious differences in interpretation having in mind the purpose for which the aviation model is intended.

Both models are useful for detecting acquired colour blindness (central scotomata) caused by toxic amblyopia. Thus if a candidate passes using the large aperture but fails with the smaller aperture, this can be due to congenital colour blindness, but it may also be an indication of a central colour scotoma. In the latter case the colour weakness is accompanied by a subnormal visual acuity, and it may be necessary to shorten the distance of 6 metres normally required for the test. Also a slight shifting of the eyes may enable the observer to recognise the colour. Confirmatory diagnosis can easily be obtained by using the Bjerrum screen or alternative device for mapping the scotoma.

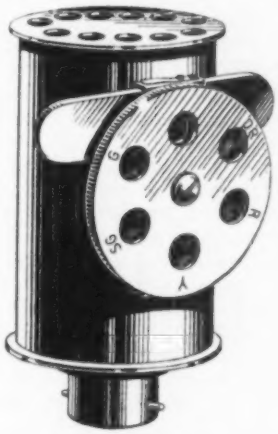


FIG. 2— Regular Model

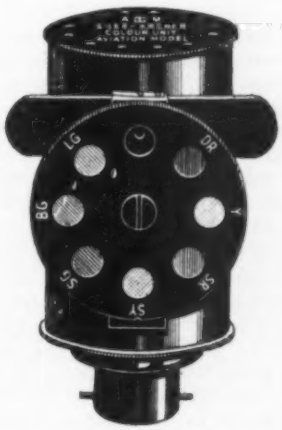


FIG. 3— Aviation Model

FIG. 2 and 3— The Giles–Archer Colour-perception Unit

MATCHING TESTS

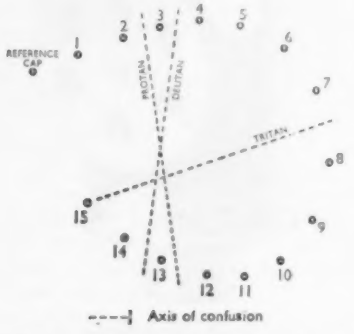
The Farnsworth Dichotomous Test D 15

This is one of a number of simplified tests on the lines of the original Farnsworth–Munsell 100-hue test, which has already been described in this *Journal* [11].

The 85 standard colours in the original test are reduced to 16 coloured plastic caps (including a reference cap) which have been skilfully chosen so as to give an approximately equally spaced chromatic circle based on the C.I.E. chromaticity diagram.

The reference colour cap is fixed permanently at one end of the rack (1 in. × 2 in. × 15 in.) consisting of two hinged wooden panels, and the subject is asked to select from the remaining numbered caps the one nearest in hue to this reference cap. Then from the remaining 14 caps he selects the one nearest to this, and so on until all the chips have been arranged in order.

The method of interpreting the results is similar to that which is used in the 100-hue test, i.e. the responses are plotted on a special diagram using a circular pattern in counterclockwise order beginning with the reference cap and continuing with No. 1–15. Starting at the point on the diagram marked "reference cap", the responses are joined in straight lines in the order in which they were recorded.



[FIG. 4—The Farnsworth Dichotomous Test]

Persons with normal colour vision show no, or scarcely any, errors in the correct sequence, and even when they do, the chords joining consecutive numbers lie close to the circumference of the circle. Protanopes make more errors, and the chords slope upwards towards the left in a S.E. to N.W. direction, whereas with deuteranopes the chords slope towards the right, i.e. S.W. to N.E.

It is pointed out that, although the usual pseudoisochromatic tests can indicate whether a person's colour vision is defective or not, they do not differentiate between a slight colour weakness and a severe one. The Dichotomous Test claims to be able to pick out from the above colour-defectives those whose deficiency is such that it might be expected to give rise to practical difficulties. Thus it can be used as a vocational test to eliminate dichromats who cannot be relied upon to distinguish between coloured lights, cords, cables, etc., which are used in many industries. Yet it will admit quite a large class of slightly abnormal colour-blind persons who can make sufficient colour discriminations for many routine jobs in various branches of industry.

It is estimated that a typical pseudoisochromatic test designates 8–9% of the ordinary male (U.S.A.) population as not normal. This figure is in close accord with that given by Wain [12], who found 9·3% of colour-defectives after testing 409 males using the Ishihara test. In each case the given percentages relate to colour-vision defects ranging from a slight colour weakness to severe colour blindness, without any distinction as to the degree of defect. The Dichotomous Test picks out only 4·6% of colour-defectives, but these are the serious cases which are likely to prove troublesome in many occupations that require some colour discrimination.

The Wain Dichroic-ladder Test

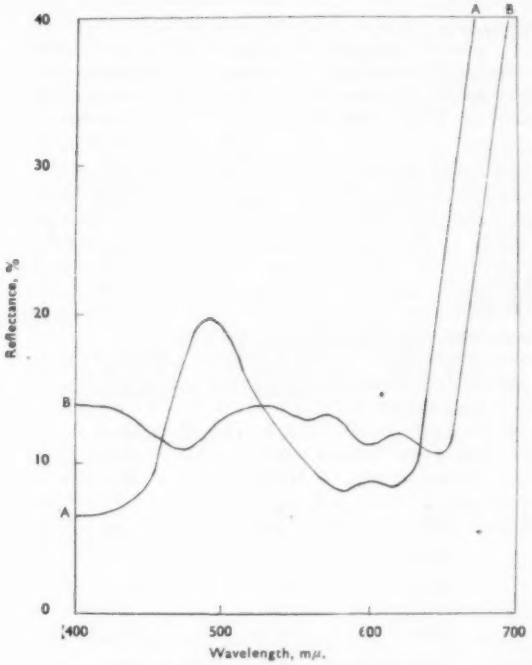
This test has been developed from the Wilson test [13], and it is likewise based on the use of metameric matches.

Although the change in colour shown by some dyed materials when viewed under different illuminants is a very familiar phenomenon, it is not easy to give a simple explanation for it.

The reflectance curve of the dyed surface gives some indication of the likelihood of any such alteration taking place. As a general rule, those surfaces which show fairly constant reflection throughout all wavelengths do not show such changes in hue. On the other hand, a reflectance curve showing high peaks, particularly in widely separated parts of the spectrum, indicates a marked alteration in shade in artificial light. This is illustrated in Fig. 5, which shows the reflectance curves of two green patterns used in the Wain test: *A* is much redder in light from a tungsten-filament lamp than in daylight, whereas *B* shows scarcely any change. A similar effect is illustrated in Fig. 6, in which a blue surface having a smooth broad reflectance curve shows no alteration in artificial light. The yellow surface, which has a sharp reflectance peak, turns greener in tungsten light.

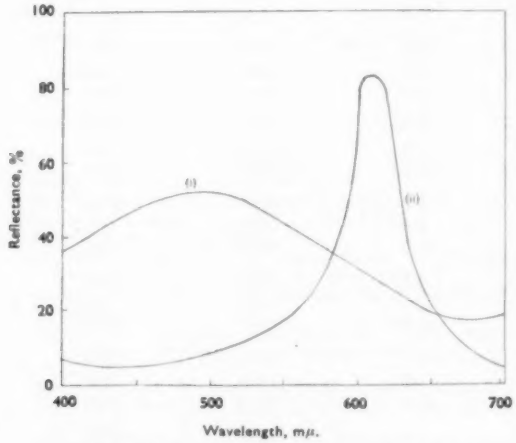
Recently Guthrie and Oliver [14] give an interesting example of two browns on cotton which show reversal of colour under different illuminants. In tungsten light one pattern is redder than the other, whereas in light from a colour-matching fluorescent lamp these effects are reversed. The pattern which has much higher reflectance in the extreme red region is redder in tungsten light, which has a high emission in this region. Using the fluorescent lamp, where most of the radiation is below 630 mμ., the other pattern appears redder, as it has higher reflectance in these regions.

Any change of hue in artificial light is also influenced by the general adaptation of the eye to artificial illuminants. After long exposure to such a light source as a tungsten-filament lamp, the colour of a dyed surface tends towards its appearance in daylight, as the eye tends to adjust itself to cancel out the deficiencies of the light source. In fact the actual colour of a dyed material in daylight and artificial light is not entirely constant, but varies according to the way in which the eye adapts itself to the illuminant. It has been pointed out that, but for this compensatory effect, a white material illuminated by artificial light would appear extremely yellow. The adaptation of the eye to artificial daylight is probably due to a slight shift in the sensitivities of the eye receptors for colour. As each of the three receptors—red, green, and blue—operates roughly over one-third



(A) Redder and flatter in artificial light
(B) No alteration in artificial light

FIG. 5—Two Green Dye Mixtures showing Different Behaviour in Tungsten Light



(i) Blue surface which does not alter in artificial light
(ii) Yellow surface which turns greener in artificial light

FIG. 6—Two Typical Reflectance Curves illustrating Different Colour Behaviour in Tungsten Light

of the spectrum, the net result is that the illuminant colour appears almost white. Broad and gentle reflectance curves will naturally show far less change in artificial light than sharp peaks, as this mechanism is less likely to be capable of adjustment in the latter cases.

In the case of tungsten light, which is richest in the far red emission, the eye tends to become most sensitive to blue wavelengths, where the light emission is weakest, less so to green, and least sensitive to red. This is one reason for the alteration in the shade of material dyed with triphenylmethane acid blues, e.g. Disulphine Blues, in tungsten light. The change is to a bright emerald green, and not to a duller colour resulting from the excess red and far red emission acting as complementary to the blue–green.

Change of colour in artificial light was used in the Wolfflin diagrams [15], which have been criticised [5] as being of only limited interest, viz. for the detection of varying degrees of red-blindness. Persons having such characteristics are known from a study of luminosity data (Fig. 1) to be less sensitive to red radiations compared with those whose colour vision is normal or who have some kind of green-blindness. The two latter groups have no difficulty in reading the figures in the Wolfflin diagrams either in daylight or in artificial light. Protanopes or protanomalous persons, on the other hand, experience difficulty with the figures under artificial light, although not in daylight.

Garner [16] also modified and expanded the idea of using metameric matches and devised a test which is quite sensitive and which is capable of detecting the various kinds of defective colour vision including the slight "blue-blindness" brought about by excessive macular pigmentation.

In constructing the Wain Dichroic-ladder Test, a wool pattern, called a *floater*, was dyed with a mixture of acid dyes chosen on account of the appreciable change in hue shown when moved from daylight into tungsten light. A series of patterns was then prepared using a mixture of metal-complex (1 : 1) dyes which show little or no change in hue when moved from one illuminant to another. Each series consists of 10–12 dyeings, and the extremes correspond roughly to the matching of the floater as seen by a normal observer using a daylight matching lamp and using tungsten light. In fixing the intermediate patterns, an attempt was made to obtain equal hue steps between each pattern and also to keep the lightness level constant. Several ranges (floater with corresponding series of matchings) were tried out, and finally four were selected. The four floaters were—green (with series of dyeings ranging from yellow–grey to green), blue (with series ranging from dull violet to blue–green), red (with series ranging from red to brown), and violet (with series ranging from purple to blue–grey).

Experimental

All dyeings were carried out on Botany serge scoured at 40°C. with Lissapol N (ICI) and thoroughly rinsed free from detergent.

The four floater patterns were dyed with mixtures of level-dyeing acid dyes applied in the usual way from a dyebath containing Glauber's salt and sulphuric acid. The corresponding series of dyeings were dyed with mixtures of three Neolan dyes, using 8% sulphuric acid on the weight of material. A burette was used for measuring the required amounts of dye solutions, and the quantities given in Table I are stated in millilitres, each millilitre representing 0·01% dye on the weight of material.

TABLE I

Floater Patterns

Dye	*Colour Index* Designation	I (Green)	II (Blue)	III (Red)	IV (Violet)
Lissamine Fast Yellow 2GS	C.I. Acid Yellow 17	30	15	—	—
Lissamine Fast Violet 2BS	C.I. Acid Violet 41	40	50	—	—
Disulphine Blue AS	C.I. Acid Blue 5	—	—	6·5	—
Disulphine Blue VS	C.I. Acid Blue 1	—	—	6·5	—
Lissamine Green BS	C.I. Acid Green 50	—	—	—	42·5
Naphthalene Scarlet RS	C.I. Acid Red 26	—	—	37·0	24·0

TABLE II

Series of Shades

Pattern No.	Component	Amounts (ml.) of Red, Yellow, and Blue			
		Series I Yellow–Grey to Green	Series II Dull Violet to Blue–Green	Series III Red to Brown	Series IV Purple to Blue–Grey
1	Red	16·7	23·15	67·5	32·0
	Yellow	14·0	—	3·7	1·9
	Blue	26·0	31·8	11·85	28·8
2	Red	15·0	21·1	64·6	31·0
	Yellow	15·0	0·6	4·75	2·3
	Blue	27·2	33·55	12·9	29·1
3	Red	13·35	19·05	61·7	30·0
	Yellow	16·0	1·3	5·8	2·7
	Blue	28·5	35·3	13·9	29·4
4	Red	11·7	17·0	58·8	29·0
	Yellow	17·0	2·0	6·85	3·1
	Blue	29·6	37·05	14·95	29·7
5	Red	10·0	14·95	55·9	28·0
	Yellow	18·0	2·7	8·95	3·5
	Blue	30·8	38·8	15·95	30·0
6	Red	8·35	12·9	52·0	27·0
	Yellow	19·0	3·4	10·0	3·9
	Blue	32·0	40·5	17·0	30·3
7	Red	6·7	10·85	49·1	26·0
	Yellow	20·0	4·1	11·05	4·3
	Blue	33·2	42·25	18·05	30·7
8	Red	5·0	8·8	46·2	25·0
	Yellow	21·0	4·8	12·15	4·7
	Blue	34·4	44·0	19·05	31·0
9	Red	3·35	6·75	43·3	24·0
	Yellow	22·0	5·5	13·2	5·1
	Blue	35·6	45·75	20·1	31·3
10	Red	1·7	4·7	40·4	23·0
	Yellow	23·0	6·2	14·3	5·5
	Blue	36·8	47·6	21·15	31·7
11	Red	—	—	37·5	22·0
	Yellow	24·0	—	15·35	6·0
	Blue	38·0	—	22·15	32·0
12	Red	—	—	34·6	21·0
	Yellow	—	—	16·4	6·4
	Blue	—	—	23·2	32·3

The three Neolan (Ciba) dyes used were Red BRE (C.I. Acid Red 212), Yellow GR (C.I. Acid Yellow 99), and Blue 2G (C.I. Acid Blue 158A), the proportions employed being given in Table II.

The method of testing was to mount each series in a frame set at an angle of 45° to the light from a Siemens colour-matching unit FTF 2444, and to slide the floater along the frame until a match was made. The observer was asked to match to the nearest pattern in the series, and its number was then noted, but in a few instances matches were made between two adjoining patterns. A few observers complained that, although they could give an approximate match, the hue of the floater was

just outside that of the series. The majority of observers experienced no difficulty in this connection, and the problem arises only because the test is so extremely sensitive to very slight variations in individual colour vision that it was found impossible to devise a matching range to suit everybody.

The Wain test was used to examine the colour vision of 409 young people, in conjunction with the Ishihara test, which classed 371 observers as normal and 38 as having defective colour vision. Using the Wain test, many of the 371 normal observers showed variations in the matching positions in the various ranges. Also, the 38 persons who failed to pass the Ishihara test gave results with the Wain test which divided them into three groups each having a different kind of colour-vision defect. A detailed analysis of the results of the investigation will be given in a separate communication [12], but although further work must be carried out in order to give a fuller assessment of the value of the Wain test, it is already clear that it is extremely sensitive for detecting slight deviations from normal colour vision.

* * *

The authors thank Mr. E. Wilson, of the Bradford Dyers' Association Ltd., for valuable advice and assistance at the beginning of the investigation; Dr. G. R. Ramage and Dr. E. Tittensor, former and present heads respectively of the Department of Chemistry, Colour Chemistry, and Dyeing, for their interest and encouragement; also R. Archer & Sons Ltd. for the loan of blocks.

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(*MS. received 14th May 1959*)

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Discussion

Dr. G. R. RAMAGE: Are normal persons, as well as abnormal persons, able to reproduce matching results previously obtained?

Mr. JORDINSON: Our tests indicate that all persons always match the floater patterns at the same point in the appropriate series.

Mr. G. ENGLAND: When young people are tested by the Wain test, which sex gives most normal results?

Mr. JORDINSON: One would expect the female sex to have more normal colour vision than males. The Wain test is sufficiently sensitive to show slight deviations from normal colour vision in females.

Mr. ENGLAND: Is it true that an older person sees only half the amount of light seen by a much younger person?

Mr. JORDINSON: On account of the variation between individuals in regard to macular pigmentation and yellowing of the lens of the eye, it is not possible to give precise figures, but much blue light (440–520 mμ.) is cut off owing to these defects in older people. The effect is partly rectified by adaptation and increased luminosity.

Dr. H. H. GOLDTHORPE: Can the startling and futuristic expressions of modern art be due to the artist seeing colours differently from other people?

Mr. JORDINSON: There is no reason to assume that an artist's colour vision is any different from that of other people. As a result of their training in the use and appreciation of colour, artists sometimes express their colour sense in unusual forms.

Mr. B. BAMFORTH: Can a person go through life totally colour-blind without knowing it?

Mr. JORDINSON: The more serious the defective colour vision, the more likely a person is to be aware of it, and it would seem impossible for a totally colour-blind person to be unaware of the defect. Slight deviations from normal colour vision may well pass unnoticed, particularly if the person's occupation demands little or no colour discrimination.

Mr. R. RAW: If it is true that colour-matching defects are inherited, cannot skill in matching also be inherited?

Mr. MINSHALL: Training and experience in colour matching are of far greater importance than any inherited colour discrimination.

Mr. F. DYSON: Are the figures in certain plates of the Ishihara test visible only to a colour-defective? If a person has spent several years observing relatively minute variations in colours, e.g. a practising dyer, is it possible that he might be able to trace out the figures in the above plates?

Mr. JORDINSON: In four plates of the 9th edition of the Ishihara test, red–green blind persons can read the figure (or figures) which cannot usually be seen by persons of normal colour vision. We have come across a few cases where persons having normal colour vision have been able to read the "hidden numbers", and other investigators have reported similar instances. Training in colour discrimination may well enable such people to pick out these numbers more easily.

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Xenon-arc Fading Lamps

K. McLaren

The first two models of commercially available fading lamps based on xenon arcs have been studied to determine how closely they approach the conditions necessary to duplicate an average daylight exposure in the United Kingdom. Modification of the original lamp design is necessary to obtain the required effective humidity.

Introduction

The light fastness of a coloured material is determined by exposing it to light together with eight blue wool standards. The official method, *B.S.* 1006 : 1955, specifies daylight as the light source, but because this is inevitably slow, particularly in winter, fading lamps are widely used. Investigations carried out in recent years [1] suggest that a fading lamp will give the same result as a daylight exposure if the nature of the light closely resembles daylight through window glass, and the temperature and the moisture content of the specimen during exposure are equal to the average values occurring in a daylight exposure. Average values for the United Kingdom have been published [2] and are not difficult to obtain in a well designed lamp, but until recently it was not possible to meet the first requirement, namely that the light source should resemble daylight.

In 1947 a new light source called the "gas arc" was introduced; this consisted of a xenon gas discharge lamp in quartz operated at relatively high current density. Both in spectral composition and in attainable illumination level the light emitted was found to be much closer to daylight than with any artificial light source (e.g. carbon arc or mercury vapour lamp) previously available. In 1951 Boulton and Guthrie recommended that consideration should be given to its use in fading lamps [3]. In 1954 the first fading lamp based on a xenon arc (as the "gas arc" is better described) was marketed by Quarzlampen G.m.b.H., Hanau, Germany, which was the outcome of collaboration between this firm and Casella Farbwerke Mainkur [4]. Two such lamps are marketed today—the Xenotest PL 393, which employs a wet-wick system for humidification, and the Xenotest-W (PL 394), which has in addition four jets for more efficient humidification, and two for spraying the specimens if fastness to weathering is required. Both the PL 393 and the PL 394 have been thoroughly studied, and this paper describes the investigation in some detail.

Experimental

From an earlier investigation it was deduced that the maximum correlation with daylight exposures made in the United Kingdom would be obtained in a fading lamp which satisfied the following criteria—

(*a*) The actinic radiation falling on the patterns (specimens and standards) must be similar in spectral characteristics to daylight passing through window glass [5]

(*b*) The surface temperature of the patterns must be 120 ± 15°F.[1]

(*c*) The effective humidity, i.e. the relative humidity of the air in contact with the exposed surface of the patterns, must be about 20% [2].

It will be most convenient to discuss both types of lamp under these headings.

A— SPECTRAL CHARACTERISTICS

The emission spectrum of the xenon arc is in part discontinuous, but the lines are not only very close together, but are also accompanied by continuous radiation of comparable intensity extending from 200 to 1,100 mμ. In both Xenotest lamps, the radiation from the arc passes through a "cuvette", a double-walled glass cylinder through which cold water passes, the glass absorbing all radiation below 295 mμ., the limit of solar radiation at the earth's surface. Fig. 1 (reproduced from the pamphlet published by Quarzlampen G.m.b.H.) shows the spectral characteristics of the light falling on the patterns in the Xenotest compared with daylight at sea level.

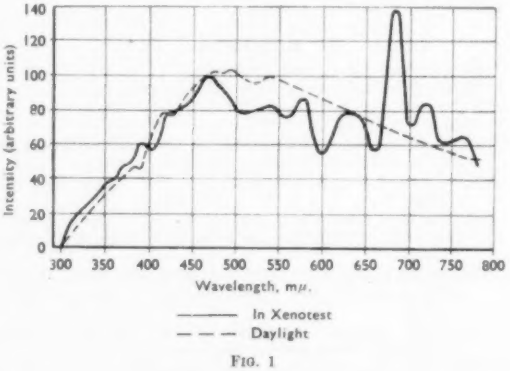

FIG. 1

Window glass as used in the daylight test, however, absorbs all radiation below 330 mμ., and therefore for maximum correlation with the daylight test a similar filter should be placed between the arc and the patterns. It can be argued, however, that, whilst the daylight test conditions are correct for materials which are usually behind window panes, e.g. curtains and upholstery fabrics, they are wrong for materials such as suitings, dress fabrics, etc., which are frequently exposed in the open. It is even possible that, had transparent

plastics with better ultraviolet-transmitting properties existed 30 years ago, when the basic principles of the daylight test were being worked out, they might have been specified instead of window glass. However, because of the vast amount of data accumulated from exposures made behind window glass, the Colour Fastness Subcommittee of ISO (ISO/TC 38/SC 1) specifies that a window-glass filter must be inserted between the arc and the patterns in xenon arc lamps[6]. The most convenient method of doing this is to insert strips of window glass inside the cuvette.

It should be stated, however, that there are very few dyes which are sufficiently sensitive to this radiation (which amounts to only 0·25% of solar radiation at sea level) for serious discrepancies to occur with and without window glass. Toepffer has recorded[4] that C.I. Acid Orange 3 is rated 3–4 in the normal Xenotest and 5–6 if a window-glass filter is inserted in the system.

B— SURFACE TEMPERATURE

Both Xenotest lamps contain a built-in thermometer which measures the air temperature in the exposure chamber. In 1954 Norton[7] showed, however, that control of the air temperature did not ensure constant conditions, as it was quite possible for the same material in two lamps having the same air temperature to differ widely in surface temperature. The AATCC therefore specified black-panel temperature control, as it is a much more reliable guide: this has also been adopted by the ISO Colour Fastness Subcommittee, and the temperature specified is 131 ± 9°F., as this appeared to be a reasonable average for daylight exposures in Northern Europe.

Black-panel temperatures in this range can be easily maintained, provided that the air filters are not allowed to become clogged and the light–dark cycle mechanism is operating. This device automatically turns the patterns away from the light every other revolution, presumably to simulate the effect of night and day; it does not, however, achieve this aim. Whilst fundamental photochemical studies have shown that a reaction induced by exposure can proceed in the dark, there is little evidence that this can have any significant effect in routine light-fastness testing; the only effect of night is that the temperature falls, the relative humidity rises, and the moisture content of the pattern increases.

This effect is obtained in the latest Fade-Ometer, Model FDA–RC; after 3·8 hr. exposure, the light is automatically switched off and the air humidity raised to 85–95% for 1 hr. This re-absorption of moisture in the dark cannot occur during the dark cycle in the Xenotest, however, because the pattern is in the dark for only 12 sec., and this is much too short a period for sufficient cooling to occur. The light–dark cycle is effective, however, in limiting the temperature build-up, for black-panel temperatures are about 40°F. higher when it is not operating.

It is important to note the marked difference between the Xenotest and carbon arc fading lamps with respect to black-panel temperatures. When there is a water screen between the carbon arc and the patterns, this has the effect of reducing the black-panel temperatures by 50–60°F.; black-panel temperatures in such lamps are invariably no more than 10°F. higher than the temperature of the air. Both Xenotest lamps similarly contain a water screen, but black-panel temperatures are usually 40–50°F. higher than air temperatures, even with the light–dark cycle operating, in spite of the fact that the flow of cooling air is much greater than in carbon arc lamps.

The reasons for this are very interesting. Water begins to absorb infrared radiation at 800 mμ., the intensity and the width of the absorption bands increasing as the wavelength increases. The infrared radiation from the enclosed carbon arc extends evenly from 700 to at least 3,000 mμ., so that the bulk of it is strongly absorbed by water. That from the xenon arc, however, although producing at least as much heating effect on the specimen, extends to only about 1,000 mμ., and is therefore only slightly absorbed. The inefficiency of the water screen in the Xenotest for reducing black-panel temperatures can be a defect, as will be seen later.

C— EFFECTIVE HUMIDITY

Fading occurs at the surface of a pattern, and therefore the black-panel temperature is more relevant than the temperature of the ambient air. Similarly, the relative humidity of the ambient air is not the important factor, it being necessary to control the relative humidity of the air in contact with the surface of the pattern. This humidity is termed the *effective humidity*, and to duplicate daylight exposure conditions in the United Kingdom lamps should be operated at an effective humidity of 20%[2].

The effective humidity is calculated by means of a psychrometric chart from the air temperature, the relative humidity and the black-panel temperature, all of which are readily obtained, the first two from instruments built into the lamps and the third by mounting a black-panel thermometer on a Xenotest frame.

Xenotest PL 393

In this lamp, the air temperature is reasonably constant at 85°F., whilst the black-panel temperature should be between 122° and 140°F.[6]; the relative humidity required to give the desired effective humidity is 67% at 122°F. and 100% at 135°F. It is generally recognised that an ordinary wet-wick system of humidification cannot produce a relative humidity above 50%, especially in the Xenotest, where air at room temperature passes over the wicks and may be heated up in the exposure chamber. The effective humidity in the Xenotest PL 393 is therefore too low to duplicate average United Kingdom daylight conditions, and this was confirmed by the exposure of humidity-sensitive specimens.

Xenotest PL 394

In this lamp, the humidity of the air in the exposure chamber is increased by the provision of four jets which spray water into the chamber. A

hygrometer is inserted in the chamber, and the movement of its needle switches the spraying device on or off, according to whether the humidity is below or above a value which can be preset between 0 and 100%.

With the maximum setting of 100% R.H. at an air temperature of 85°F. the effective humidity will be 30% at 122°F. and 18% at 140°F. black-panel temperature, suggesting that the desired conditions could be obtained. However, the exposure of a number of sensitive specimens in a lamp operating under these conditions showed conclusively that the effective humidity was much less than 20%.

This was particularly disconcerting, as it appeared to cast doubt on the validity of the effective humidity concept. However, a possible explanation was soon forthcoming: the arrangement of the jets was such that the boosting effect occurred *after* the air had passed over the exposed face of the patterns, so that during the exposure period the air had the same humidity as in the Xenotest PL 393. This was confirmed by placing sensitive specimens nearer the back of the chamber, i.e. away from the point where the unboosted air comes in; this showed that the effective humidity was at least 20%.

This supported the criticism of L. F. C. Friele (*Personal Communication*) that it would be better if the boosting jets had been placed underneath the floor of the exposure chamber, so that boosting occurred before the air passed over the patterns. This was easily done, but unfortunately, although it increased the effective humidity to at least 20%, it also produced a marked humidity gradient from the bottom to the top of the exposure frame, and therefore the ideal positioning of the jets is still to be ascertained. H. Toepffer (*Personal Communication*) has found that the jets should be both above and below the floor of the exposure chamber.

Whilst it is well established that an effective humidity of 20% is required, and that this can be obtained from an air humidity of 100%, it must be admitted that such conditions are very artificial, particularly as the air is not only saturated, but also contains suspended droplets; therefore it might be preferable to achieve the desired effective humidity at a lower relative humidity, by reducing the difference between the air temperature and the black-panel temperature. Toepffer has suggested an ingenious way of doing this: strips of infrared-absorbing glass were placed in the water in the cuvette, and this lowered the black-panel temperature considerably. These particular filters also had the ultraviolet transmission characteristics of window glass, thus effecting two improvements simultaneously.

Conclusions

There are three criteria which must be fulfilled if the maximum correlation between a fading-lamp exposure and an average United Kingdom daylight exposure is to be obtained: these concern spectral characteristics, temperature, and effective humidity. The xenon arc can be easily filtered to give light practically equivalent to daylight or to daylight transmitted by window glass.

The temperature of the surface of the patterns in both Xenotest PL 393 and 394 varies according to the amount of dust absorbed by the air filters and whether the light–dark cycle mechanism is operating: the minimum temperature is about 120°F. Present knowledge indicates that the optimum temperature, i.e. that for maximum correlation with daylight exposure, is between 120° and 170°F.

The effective humidity in the PL 393 is not much more than 5%, which is too low to duplicate daylight exposure in the United Kingdom. In spite of the atomiser humidity boosters in the PL 394, the maximum effective humidity is still well below 20%. The ideal conditions can probably be obtained either by resiting the jets or by inserting an infrared-absorbing glass filter in the system, or by both methods.

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Variations in the Assessment of Light-fastness Exposures

K. McLaren

Ten specimens exposed against the light-fastness standards have been assessed by 72 observers by the method described in *B.S.* 1006:1955. The results are expressed in conventional statistical terms, and their significance is discussed. The most important factor affecting the agreement among assessors was off-tone fading, which caused a considerable reduction in agreement. The amount of experience the assessor possessed was generally quite unimportant.

Introduction

The standard method of determining the colour fastness to daylight of coloured textiles [1] requires the exposure of a specimen and eight blue wool standards so as to produce one, two, or three different degrees of colour contrast on the specimen. The assessor has then to compare this overall visual contrast with the varying degrees of contrast on the standards and to decide which is nearest to the specimen: the light fastness of the specimen is the number of this standard.

Such observations are, therefore, subjective, and differences between observers must be expected. Only one investigation into this essential part of light-fastness testing has been published, that by Bülow and Horrdin [2], but they used the AATCC method of exposure and assessment, and their claim that the results would be equally applicable to the ISO method was challenged by the author [3]. It was, therefore, highly desirable that a similar investigation into the degree of agreement among assessors of specimens exposed by the ISO method should be undertaken.

Experimental

To save time, specimens and standards were not specially exposed but were selected from routine exposures made by Method 2 of *B.S.* 1006:1955. This method requires only one set of standards for a large number of specimens, but for the purpose of this investigation one exposed specimen was detached and remounted above the standards exposed simultaneously. Each specimen and relevant standards had, therefore, been exposed for three different periods, and in general there were three different degrees of fade on each. These exposure cards were undoubtedly typical of routine light-fastness assessments made throughout the world, apart from the U.S.A.

The choice of specimens was governed by the desire to cover as widely as possible the following variables—

(*a*) Light fastness
(*b*) Hue
(*c*) Depth
(*d*) On-tone and off-tone fading
(*e*) Fibre and fabric structure.

To cover these adequately would have required a very large number of specimens, which would have prolonged the investigation unduly; it was, therefore, decided to limit the number of specimens to 10, and they are described in Table I.

The 72 assessors were chosen mainly from the laboratories associated with five members of the Society's Light Fastness Subcommittee, and these were divided into three categories based on the number of exposures they had assessed before they took part in this investigation—

(*a*) Experienced (49 assessors)	>100 assessments
(*b*) Moderately experienced (12 assessors)	10–100 assessments
(*c*) Inexperienced (11 assessors)	<10 assessments

They were asked to assess the specimens in accordance with *B.S.* 1006, the only difference being that, because the spacing between standards 6 and 7 is greater than that between any other

TABLE I

Specimen No.	Hue	Depth	Fabric	Light Fastness*	Nature of Fade
1	Red	2/1	Mercerised poplin	4–5	On tone
2	Violet	1/1	Terylene	2	Very much redder
3	Brilliant blue	1/1	Cotton limbric	7–8	On tone
4	Red	1/2	Mercerised poplin	5–6	On tone
5	Orange	1/3	Linen	5–6	On tone but duller
6	Red–violet	1/1	Viscose sateen	6–7	On tone
7	Yellow	1/3	Cellulose acetate sateen	4–5	Somewhat redder
8	Blue	1/3	Wool flannel	5–6	On tone
9	Black	2/1	Cellulose acetate sateen	3–4	To a brown
10	Green	1/2	Mercerised cotton sateen	5	On tone

* Mean of all the assessments made rounded off to nearest half-grade.

TABLE II

Assessments by Different Categories of Assessors

Specimen	Mean Light Fastness			Standard Deviation			Overall
	(*a*)	(*b*)	(*c*)	(*a*)	(*b*)	(*c*)	
1	4·7	4·4	4·6	0·34	0·56	0·55	0·41
2	2·0	1·9	2·7	0·66	0·48	0·85	0·65
3	7·6	7·4	7·8	0·22	0·64	0·25	0·32
4	5·4	5·5	5·5	0·53	0·50	0·52	0·57
5	5·6	5·8	5·6	0·56	0·45	0·39	0·51
6	6·4	6·2	6·2	0·40	0·49	0·39	0·40
7	4·7	4·7	4·6	0·72	0·75	0·90	0·74
8	5·5	5·5	5·4	0·59	0·52	0·49	0·55
9	3·6	3·7	3·6	0·47	0·71	0·45	0·54
10	5·2	5·3	5·4	0·47	0·49	0·68	0·49
			Average	0·52	0·57	0·58	0·53

adjacent standards, the following grades were permitted in this region— 6, 6–7 (nearer 6), 6–7, 6–7 (nearer 7), 7.

Results

The 720 assessments obtained are not of sufficient general interest to warrant publication, but they are available for consultation by any interested person. The results of elementary statistical analysis are given in Table II.

Discussion of Results

GENERAL

The average overall standard deviation is 0·53 or half a light-fastness grade. This means that, providing the assessors chosen were a representative sample of the population (and there is no reason to think they were not, although their number was far too small for one to be certain that they were) and the specimens were also representative (see p. 597), then two-thirds of all assessments made will be not more than ½ grade away from the mean value, 95% will be not more than 1 grade away, and less than 1% will be more than 1½ grades away. The mean value must be assumed to be the true value, as there is no other possible criterion; the validity of this assumption is strengthened by the fact that the frequency distribution of the assessments of all specimens was normal or Gaussian.

It is helpful also to compare this standard deviation of 0·53 with the values found in two other statistical analyses of fastness assessments. In the assessment of staining using the Staining Scale (the easiest visual task in fastness testing) the standard deviation was found to be 0·30[4], and in the assessment of specimens which change in hue and/or brightness with and without an accompanying loss in depth (the most difficult task) the standard deviation was 0·52[5].

Bülow and Horrdin[2] found a standard deviation of 0·33 among assessors of light-fastness exposures, and the results now obtained clearly refute the author's original contention[3] that the ISO method should give better agreement among assessors than the AATCC method. However, whilst the difference in standard deviations (0·33 against 0·52 for experienced assessors) is great enough to indicate a real difference in the amount of agreement among assessors, it cannot be assumed that this is due solely to the difference in methods, because different specimens and different assessors were used in the two experiments.

EFFECT OF EXPERIENCE

The average standard deviation for the three classes of experience is as follows—

>100 assessments	0·52
10–100 assessments	0·57
<10 assessments	0·58

and these differences clearly show that the effect of experience is surprisingly slight. This view is supported by the fact that for two of the specimens the standard deviation for the experienced group is very much greater than that for one of the less experienced groups—

SPECIMEN NO. 2	
Moderately experienced	0·48
Experienced	0·66
SPECIMEN NO. 5	
Inexperienced	0·39
Experienced	0·56

No explanation of this conclusion seems possible from the available data.

DIFFERENCES BETWEEN ASSESSORS

These were determined by the following simple and arbitrary method of scoring—

Difference from mean	0	¼	½	¾	1	1¼	1½ and over
Score	10	9	8	6	4	2	0

complete agreement on all ten specimens thus producing a score of 100, and an average of ½ grade out on each specimen 80.

The highest score was 95, reached by three experienced assessors; twelve assessors scored 90 or over, ten being experienced, one moderately experienced, and one inexperienced, although he was an expert colour matcher.

Two assessors who had never assessed an exposure before and whose experience of colour was that of "a man in the street" scored 75.

Eight scored less than 70, five of these being in the most experienced class. The lowest result was 52, but, as this assessor scored 79 on his second attempt several months later without any intervening assessments, this is probably a freak result; the next lowest result was 59.

DIFFERENCES BETWEEN SPECIMENS

In the case of the largest and most important group, the experienced assessors, the standard deviations vary from 0·22 to 0·72. In Table III these standard deviations are arranged in order of magnitude, and the 95% confidence intervals are given. The significance of this interval is that, if one standard deviation lies outside the 95% confidence interval of another, it is at least 95% certain that this indicates a real difference in the degree of agreement among assessors.

TABLE III

Specimen	Standard Deviation (experienced assessors)	95% Confidence Interval
3	0·22	0·18–0·28
1	0·34	0·28–0·43
6	0·40	0·33–0·50
9	0·47	0·39–0·59
10	0·47	0·39–0·59
4	0·53	0·44–0·67
5	0·56	0·46–0·71
8	0·59	0·49–0·74
2	0·66	0·55–0·83
7	0·72	0·60–0·91

Average Specimens

Table III shows that Specimen No. 4 can be regarded as "average", as its standard deviation, 0·53, is the same as the overall standard deviation. Specimens 5, 8, 9, and 10 also can be considered "average", as their standard deviations lie well within the 95% confidence limits of Specimen No. 4. The number of specimens involved, however, is too small to allow one to deduce that the differences between them (hue, depth, fibre, and fabric structure) do not affect agreement among assessors.

Better-than-average Specimens

Specimens No. 1, 3, and 6 gave better-than-average agreement.

Specimen No. 3 resulted in the highest measure of agreement: all the experienced assessors rated it either 7–8 or 8, and the close agreement arises from the fact that Standard 6 had obviously faded very much more than the specimen and Standard 8 showed no fading at all. This was the only instance where the light fastness appeared to effect the degree of agreement.

Specimens No. 1 and 6 faded regularly and on tone, the most important point of interest being that Specimen No. 1, which gave the second highest measure of agreement, is red; whenever it is proposed to extend the use of *B.S.* 1006 into non-textile fields, it is inevitable that the feasibility of assessing, e.g. a red specimen against blue standards, is questioned. This was once the view of the Society's Fastness Tests Committee, as attempts were made to produce red, green, and blue standards, and until 1942 red and blue standards were issued (there were insufficient green dyes to complete the green series).

Worse-than-average Specimens

Specimens No. 2 and 7 gave worse-than-average agreement, and again detailed consideration is of interest.

The standard deviation among experienced assessors of Specimen No. 7 was the highest of all—0·72—and this means that the range of light-fastness values needed to include 95% of all the assessments made is from 3–4 to 6. Among inexperienced assessors (standard deviation 0·90) the range is even greater, from 3 to 6–7.

Specimen No. 2 gave slightly better agreement, but still significantly worse than average. It is surprising to find that one can be more than 85% certain that there was a greater degree of agreement among moderately experienced assessors of this specimen (standard deviation 0·48) than among experienced assessors (0·66).

The cause of the large general measure of disagreement is undoubtedly the fact that both specimens faded badly off-tone and irregularly; Specimen No. 2 was a bluish violet which faded to a red–violet, which then faded redder and weaker, whilst No. 7 was a somewhat greenish yellow, which faded to a dull orange, which then faded weaker.

Conclusions

If the 72 assessors and the 10 specimens are typical of whole populations (and there is no reason to think either to be atypical), then two-thirds of all assessments made will be not more than ½ grade away from the true result, 95% will be not more than 1 grade away, and less than 1% more than 1½ grades away. This agreement among assessors is about the same as among observers using the Grey Scale to assess the effect on a specimen which changes in hue as the result of applying a fastness test. The agreement is greatest when the specimen has a light fastness of 7 or higher and least when it fades off-tone.

The most surprising and disturbing conclusion is that the agreement among assessors does not increase with increasing experience of light-fastness assessments.

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COMMUNICATION

The Dyeing of Cellulose Acetate with Disperse Dyes VIII—Determination of Fibre Saturation Values

C. L. BIRD, H. K. PARTOVI, and G. TABBRON

Fibre saturation values have been determined at 60° and 80°C., in presence of a dispersing agent, for 15 disperse dyes on secondary cellulose acetate. In most cases the results agree with those obtained by calculation from aqueous solubilities and partition coefficients in the absence of dispersing agent. With the more hydrophilic disperse dyes, however, e.g. those containing two *N*-β-hydroxyethyl groups, low values are obtained in presence of dispersing agent. This is attributed to adsorption of dispersing agent rendering the fibre more hydrophobic.

When a fibre saturation value is determined by means of a single dyeing carried out in presence of a large amount of commercial dye, the result may be much too high owing to (*a*) the presence of coloured impurities and shading components and (*b*) the absence of sufficient dispersing agent to stabilise the concentrated dispersion and so prevent surface adsorption of dye by the fibre.

INTRODUCTION

The work of several authors (summarised in Part IV [1]) has shown that, when cellulose acetate (or other fibre) is dyed to equilibrium with varying amounts of a disperse dye at a given temperature, a linear isotherm is obtained; i.e. Henry's law is obeyed. The isotherm (Fig. 1A(i)) terminates at the point at which both the fibre and the water are saturated, and the relationship is expressed by the equation—

$$\frac{[D]_f}{[D]_s} = \frac{[S]_f}{[S]_s} = K$$

where K is the partition coefficient, $[D]_f$ and $[D]_s$ are the amounts of dye present at equilibrium on the fibre and in the aqueous solution respectively, and $[S]_f$ and $[S]_s$ are the corresponding saturation values in the two phases.

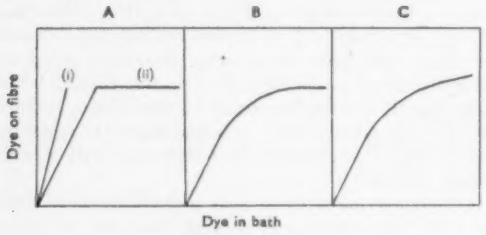


FIG. 1—Types of Isotherms

Since $[S]_f = K[S]_s$, the fibre saturation value can be calculated if the partition coefficient and the aqueous solubility for any particular temperature are known. This method was used by Bird and Harris [2], who calculated fibre saturation values for 29 disperse dyes at 80°C. on secondary cellulose acetate.

Bird and Manchester [1] obtained isotherms for five disperse dyes at 80°C. on secondary cellulose acetate. They used a fine dispersion of dye in 0·002 M. sodium 1-oleyl-4-anisidine-2-sulphonate (purified Lissapol LS). With two azo dyes they obtained curves of the type illustrated in Fig. 1A(ii). It is seen that the dispersing agent, by increasing the solubility of the dye in the aqueous phase, has reduced the partition coefficient, but the fibre saturation value is unchanged. Beyond the saturation point a third phase, viz. solid dye, is present, but increasing the concentration of the dispersion does not affect the amount of dye taken up by the fibre. With three anthraquinonoid dyes, curves of the type illustrated in Fig. 1B were obtained, but Bird and Manchester were able to show, by means of successive dyeings using a solubilisate in place of a dispersion, that the curvature near the saturation point is almost certainly due to the presence of relatively large, unreactive crystalline particles of dye, since the solubilisate gave a linear isotherm up to the saturation point.

There is, however, some tendency with all disperse dyes for additional adsorption to take place with increasing dye concentration beyond the point where the fibre has reached saturation. This occurs especially with anthraquinonoid dyes and when the amount of dispersing agent present is small. In this case a curve of the type illustrated in Fig. 1C is obtained.

Daruwalla and Limaye [3], in their study of the transfer of disperse dyes from thickener films to cellulose acetate film by steaming at 100°C., obtained isotherms for 4-nitro-4′-aminoazobenzene (purified Dispersol Fast Orange G, C.I. 11005) in the presence and absence of three different dispersing agents. They concluded that the presence of a dispersing agent affects the slope of the isotherm, but does not affect the fibre saturation value.

Some unpublished work by Miss P. Harris, however, indicates that the presence of dispersing agent reduces the fibre saturation value of 2-methoxy-4-nitroaniline→*NN*-bis-β-hydroxyethylaniline.

Vickerstaff [4] has given saturation values for 22 commercial disperse dyes on secondary cellulose acetate at 80°C. These values were obtained from single dyeings for 24 hr. in which equal weights of yarn and dye were used; the amount of Lissapol LS present was only 0·2 g./litre. Where a comparison with Bird and Harris's data was possible, we have determined the strength of the commercial dyes and converted Vickerstaff's figures into terms of pure dye, as shown in Table I. Here and in Table II the fibre saturation values are based on the oven-dry weight of yarn (the yarn used throughout this series contains 6·6% moisture at 22°C. and 65% R.H.). The calculated values for

Dispersol Fast Red R and Dispersol Fast Yellow A in Table I have been revised (as has the value for 1,4-bis-β-hydroxyethylaminoanthraquinone in Table II), for reasons which are explained later.

The position outlined above seemed to justify (*a*) further examination of the effect of dispersing agent on fibre saturation values, and (*b*) an attempt to explain the great differences between some of the observed and calculated values shown in Table I.

EXPERIMENTAL

Purified dyes and Lissapol LS, and oil-free conditioned Celanese yarn, were prepared as described in Part I [5]; fine suspensions of purified dyes were prepared as described in Part III [6]. Dyeings to equilibrium were carried out for 6 hr. or 24 hr. from a dispersion in 0·002 M. sodium 1-oleyl-4-anisidine-2-sulphonate, in a Marney dyeing machine as before. Dye on the fibre and in the dyebath was then estimated colorimetrically, the former being expressed on the weight of oven-dry yarn.

By using varying amounts of dye a series of results was obtained which enabled isotherms to be plotted [7]. The saturation value was taken to be the point where the amount of dye adsorbed by the fibre became constant (Fig. 1A(ii) and 1B). The results obtained are given in Table II.

DISCUSSION

The calculated results for 80°C. in Table II involve errors in determining both the partition coefficient and the aqueous solubility; the 60°C. calculated results are less accurate, as they involve errors in the heat of dyeing as well, so they have not been used as a basis for discussion. At 80°C. the measure of agreement between the calculated and experimentally determined results is reasonably

TABLE I

Fibre Saturation Values at 80°C.

(g./100 g. dry yarn)

Dye	C.I. No.	Vickerstaff (observed)		Bird and Harris (calc.)	
		Commercial Dye (*a*)	Pure Dye (*b*)	Pure Dye (*c*)	$\frac{b}{c}$
Dispersol Fast—					
Scarlet B 150	11110	8·3	2·1	1·8	1·2
Crimson B 150	11115	11·3	3·0	2·2	1·4
Orange G 150	11005	14·6	2·9	1·6	1·8
Red R 150	11130	24·9	2·3	1·2	1·9
Yellow A 150	10345	32·0	7·9	7·8	1·0
				Mean	1·5
Duranol—					
Violet 2R 300	61100	9·4	3·0	1·2	2·5
Red 2B 300	60710	10·8	2·1	1·1	1·9
Brilliant Blue G 300	61500	11·7	1·7	ca. 0·46	3·7
Red X3B 300	60755	12·2	2·0	1·8	1·1
Orange G 300	60700	12·3	3·7	1·0	3·7
Red G 300	60505	28·0	9·3	0·85	10·9
				Mean	4·0

TABLE II

Saturation Values for Disperse Dyes on Acetate Rayon

(g./100 g. dry yarn)

Dye	60°C.		80°C.	
	Calc.	Found	Calc.	Found
4-Nitroaniline→*NN*-bis-β-hydroxyethylaniline	0·65	0·51	1·2	1·0
4-Nitro-4′-aminoazobenzene	1·05	1·1	1·6	1·5
4-Nitroaniline→*N*-ethyl-*N*-β-hydroxyethylaniline	1·0	1·0	1·8	1·9
2-Chloro-4-nitroaniline→*N*-ethyl-*N*-β-hydroxyethylaniline	—	—	2·2	2·5
4,4′-Diaminoazobenzene	3·8	4·5	5·3	5·8
1-Amino-4-*p*-aminophenylazonaphthalene	—	—	—	7·2
2-Methoxy-4-nitroaniline→*NN*-bis-β-hydroxyethylaniline	7·4	5·6	9·9	7·7
4-Aminoazobenzene	—	—	—	17·3
2,4-Dinitro-4′-hydroxydiphenylamine	6·0	7·2	7·8	8·2
1,4-Bismethylaminoanthraquinone	—	0·24	ca. 0·46	0·34
1-Methylaminoanthraquinone	—	0·57	0·85	0·86
1-Amino-4-hydroxyanthraquinone	0·5	0·75	1·1	1·1
1,4-Bis-β-hydroxyethylaminoanthraquinone	0·61	0·59	1·06	0·80
1-Methylamino-4-β-hydroxyethylaminoanthraquinone	—	0·96	2·2	1·33
1-β-Hydroxyethylaminoanthraquinone	2·2	1·8	2·5	2·4

good, except with 1-methylamino-4-β-hydroxyethylaminoanthraquinone and the three dyes which contain two *N*-β-hydroxyethyl groups, where the observed values are appreciably lower than the calculated values.

In order to find the cause of this discrepancy, further experiments were carried out with *p*-nitroaniline→*NN*-bis-β-hydroxyethylaniline. The aqueous solubility at 80°C. given by Bird and Harris [2] was found to be too high, and the revised value (21 mg./litre) makes the calculated saturation value at 80°C. given in Table II lower than that previously reported [2]. This correction, however, did not eliminate the difference between the observed and calculated values, so an isotherm was obtained for partition in the absence of dispersing agent. Points were obtained by desorbing dyed yarn to equilibrium, and further points by means of the method described by Bird and Manchester [1] for 1-methylamino-4-anilinoanthraquinone, whereby dyed yarn is dyed further in successive lots of a saturated solution of the dye. When using this method without dispersing agent, dye is adsorbed by the glass vessel and the wire cage holding the yarn, so the solution is no longer saturated. This difficulty is overcome by omitting rinsing of the vessel and cage between successive dyeings. The isotherm is shown in Fig. 2.

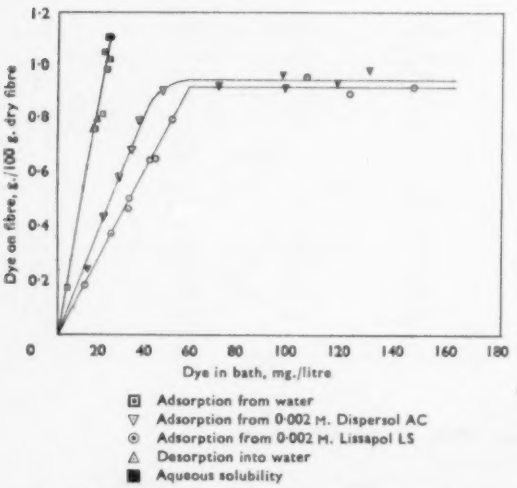


FIG. 2— Isotherms at 80°C., for *p*-Nitroaniline→*NN*-bis-β-Hydroxyethylaniline

Fig. 2 also includes isotherms obtained with dispersions in 0·002 M. Lissapol LS (from which the "observed" saturation value given in Table II is derived) and 0·002 M. Dispersol AC (ICI). The latter compound is stated by the makers to be disodium methylenedinaphthalenesulphonate. Analysis of the commercial product by the method of Barr, Oliver, and Stubbings [8] gave a mol. wt. of 470 (theoretical mol. wt. is 472). It was thought that, since Dispersol AC does not contain a long alkyl chain, it might not be adsorbed by cellulose acetate and, therefore, might not reduce the fibre saturation value. In fact it was found to be adsorbed to the extent of 1·0 m-mole/kg. at 80°C., the corresponding figure for Lissapol LS being 1·8 m-moles/kg.[1]. Isotherms (not shown in Fig. 2) were also obtained for 0·0002 M. and 0·005 M. Lissapol LS, giving fibre saturation values of 1·1 and 1·0 g./100 g. respectively. It is concluded, therefore, that the presence of dispersing agent reduces the fibre saturation value in proportion to the amount present, until the point of maximum adsorption of dispersing agent is reached.

A similar reduction in fibre saturation value, due to the presence of dispersing agent, is found with cellulose triacetate (Fig. 3). Cellulose triacetate (Courpleta) adsorbs 1·35 m-moles of Lissapol LS per kilogram of dry yarn at 90°C.

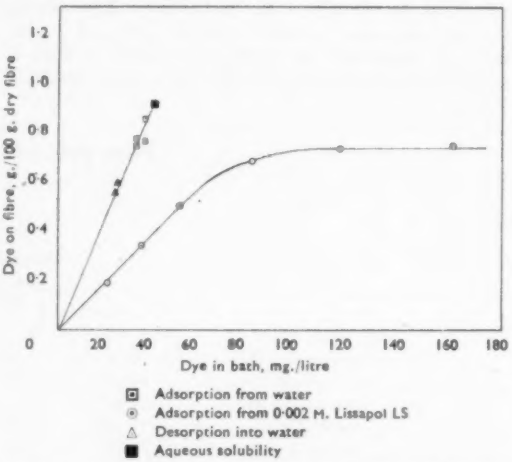
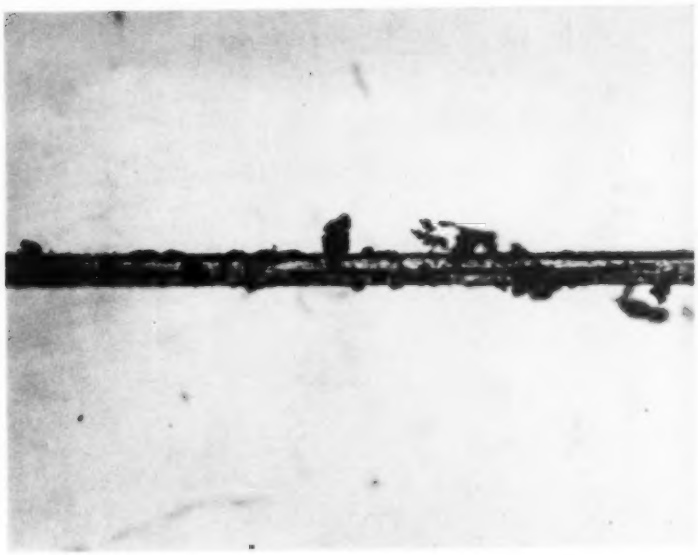


FIG. 3— Isotherms at 90°C., for *p*-Nitroaniline→*NN*-bis-β-Hydroxyethylaniline on Cellulose Triacetate

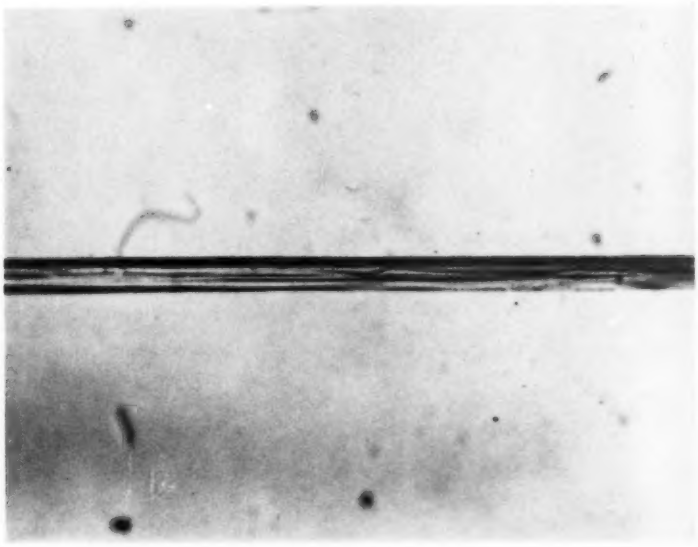
With 2,4-dinitro-4′-hydroxydiphenylamine, the original calculated fibre saturation value [2] was found to be too low, as a result of too low a value for the partition coefficient. When an isotherm was obtained from adsorption and desorption in water (as in Fig. 2), the points fell below the best straight line when the concentration of dye was low, as in the original desorption experiments. This is attributed to ionisation of this weakly acid dye in low concentration. The revised value of the partition coefficient is 625 at 80°C.

With 1,4-bis-β-hydroxyethylaminoanthraquinone the original value [2] of the aqueous solubility was found to be too low; the correct value was 61 mg./litre. The sample of dye used in the original experiments was recrystallised from ethanol; it consisted of very long fibrous needles and dissolved very slowly, both in water and in organic solvents. The sample used in the present work was recrystallised from chlorobenzene; it consisted of short thick needles and dissolved much more readily. Mixed melting point and adsorption spectra showed the samples to be alike.

The reduction in fibre saturation value due to the presence of dispersing agent occurs only with the more hydrophilic disperse dyes, e.g. those containing two *N*-β-hydroxyethyl groups. The most probable explanation of this phenomenon is that adsorbed dispersing agent renders the fibre more



(*a*)



(*b*)

FIG. 6— 1-Amino-4-hydroxyanthraquinone and Secondary Cellulose Acetate
(*a*) in absence and (*b*) in presence of Dispersing Agent

hydrophobic and so makes it a poorer solvent for the more hydrophilic disperse dyes.

When determining fibre saturation values, the indirect method of Bird and Harris [2] would appear to give more reliable values than those obtained by dyeing to saturation in presence of sufficient dispersing agent to stabilise the suspension of dye. In practice the latter method must be used with dyes of very low aqueous solubility, but these dyes do not contain *N*-β-hydroxyethyl groups and their saturation values do not appear to be affected by the presence of dispersing agent.

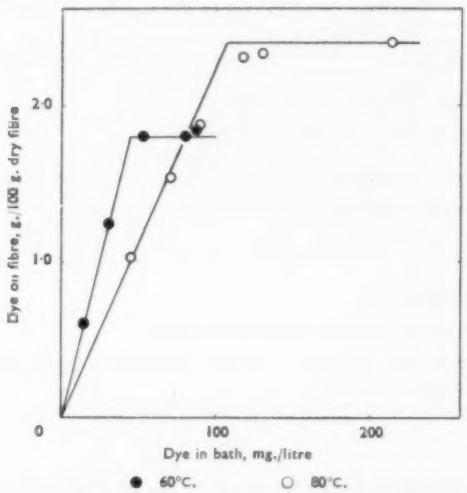


FIG. 4— Isotherms for 1-β-Hydroxyethylaminoanthraquinone

It is noteworthy that, in all cases, the fibre saturation values at 80°C. are greater than those at 60°C.; i.e. solubility in the fibre increases with temperature. On the other hand, partition coefficients decrease as the temperature is raised. This property of disperse dyes (illustrated in Fig. 4) was first shown by Schuler and Remington [9], on polyethylene terephthalate. It has recently been confirmed by Ghionis [10], who measured the fibre saturation values of 33 anthraquinonoid disperse dyes on secondary cellulose acetate.

SATURATION VALUES WITH COMMERCIAL DYES

Fig. 5 illustrates isotherms for two commercial dyes, applied in presence of only 0·2 g. commercial Lissapol LS per litre. Dye A consists of 1-methylaminoanthraquinone containing the usual amounts of impurities plus the dispersing agent used for ball-milling the crude dye. Dye B is similar, but contains about 10% of another red dye to improve its building-up property. With dye A the gradual slope is almost certainly due to increasing adsorption of dye on the surface of the fibres as the concentration of dye in the bath increases beyond the point where the fibre is saturated. With dye B the slope is much greater owing to adsorption of the second dye as well as surface adsorption of the main component. The saturation value obtained from a single dyeing will therefore depend on the amount of dye used. A large excess of dye is likely to give a value which

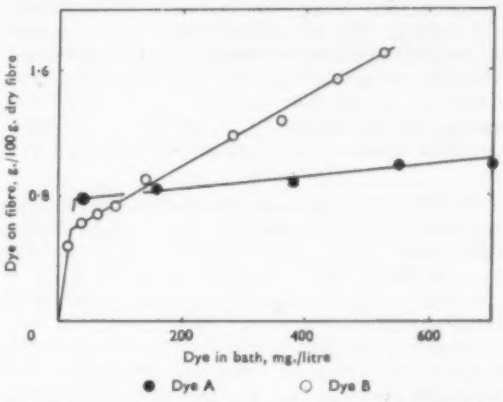


FIG. 5— Commercial 1-Methylaminoanthraquinone: Isotherms at 80°C.

is much too high (*a*) if the dye contains coloured impurities or shading components of similar hue, or (*b*) if insufficient dispersing agent is present.

The question of surface adsorption of disperse dye particles is of great practical importance. It is well known that the absence of sufficient dispersing agent gives rise to dyeings which show both poor fastness to rubbing and "specking", owing to the presence of superficial dye [11]. Bird and Scott [12] found that, with certain anthraquinonoid dyes, concentrated dispersions coagulate and precipitate on to the fibres, unless a fairly large amount of dispersing agent (2 g. purified Lissapol LS per litre) is present. This same phenomenon was observed, in the present series of experiments, with Duranol Red G (1-methylaminoanthraquinone), the fibre saturation value then being of the same high order as that given by Vickerstaff [4] (Table I).

Bird, Harris, and Manchester [6] published curves which illustrate the superficial adsorption of disperse dye in the absence of dispersing agent and the amount of dispersing agent required to prevent it. However, some uncertainty still seems to exist owing to the failure of later workers to repeat Kartaschoff's classical experiment.

Kartaschoff [13] published photomicrographs showing acetate rayon fibres coated with disperse dye particles which had been attracted to the fibres from a dispersion of the dye. Vickerstaff and Waters [14], and later Millson and Turl [15], repeated Kartaschoff's experiment, using a cell in place of a microscope slide in order to avoid mechanical trapping of dye particles by the fibres. They observed no attraction between dye and fibre, but dispersing agent was present in their experiments. We have repeated these experiments, at room temperature and at 60°C., using a 0·5 cm. glass cell and fibres of acetate rayon wound on a glass former. A rather coarse dispersion was prepared by grinding 0·1 g. pure dye and diluting to 100 ml. with distilled water. The dyes used were the weakly acid 2,4-dinitro-4′-hydroxydiphenylamine, as well as *p*-nitroaniline→*NN*-bis-β-hydroxyethylaniline and 1-amino-4-hydroxyanthraquinone. In all three cases the dye particles adhered strongly to the fibres in the absence of dispersing agent,

similar results being obtained with fibres of silk and cotton. On the other hand, when the dispersion contained 0·1 g. sodium 1-oleyl-4-anisidine-2-sulphonate per litre, there was little sign of any attraction of the particles by the fibres. These results, illustrated by Fig. 6, appear to reconcile the observations of the authors cited above [13–15].

* * *

We desire to express our gratitude to Courtaulds' Scientific and Educational Trust Fund for a scholarship which enabled one of us (G.T.) to take part in this work. Another of us (H.K.P.) is indebted to the Foreign Education Committee of Bombay and to the British Silk Dyeing Co. Ltd. for financial assistance. The dyes used were kindly supplied by Imperial Chemical Industries Ltd. Dyestuffs Division and the Yorkshire Dyeware & Chemical Co. Ltd.

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CORRESPONDENCE

The Editor does not hold himself responsible for opinions expressed by correspondents

Methods for Detection of Siroset Treatment in Wool Fabrics*

Wool fabrics treated by the Siroset procedure kindly given to us by Dr. M. Lipson, C.S.I.R.O., Geelong, Australia, as well as samples prepared at the Höhere Bekleidungsfachschule der Textilingenieurschule in Mönchen-Gladbach, Germany, have been investigated with the aim of finding reliable methods for the detection of the mixed disulphide (I) formed by disulphide exchange between wool cystine (II) and thioglycollic acid (III), as assumed by Springell [1]—

$$\underset{\text{(II)}}{\text{W–CH}_2\text{·S·S·CH}_2\text{–W}} + \underset{\text{(III)}}{\text{HS·CH}_2\text{·COOH}}$$

$$\downarrow$$

$$\text{W–CH}_2\text{·S·S·CH}_2\text{·COOH}$$

$$\downarrow \text{ Total hydrolysis}$$

$$\underset{\text{(I)}}{\text{HOOC·CH(NH}_2\text{)·CH}_2\text{·S·S·CH}_2\text{·COOH}}$$

(W = part of the wool protein).

A— INVESTIGATIONS WITH FABRICS AND FABRIC EXTRACTS

Siroset fabrics sprayed with a 0·5% aqueous solution of sodium nitroprusside and kept in an atmosphere of ammonia are immediately stained red–violet. This test proves the presence of free thiol groups, undoubtedly thioglycollic acid. Fabrics extracted with water or methanol no longer show the thiol reaction, which is now given by the extract. Quantitative analysis of aqueous extracts of Siroset-treated fabrics by the colorimetric method of Folin and Marenzi [2] showed a mixture of thiol and disulphide. Paper chromatography and spraying with chloroplatinic acid and potassium iodide [3] clearly indicated dithiodiglycollic acid (IV).

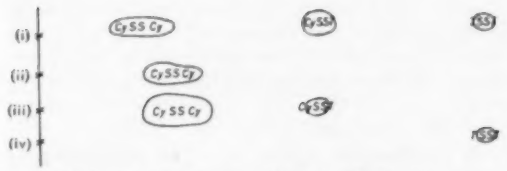
$$\text{HOOC·CH}_2\text{·S·S·CH}_2\text{·COOH}$$
(IV)

Thioglycollic acid present in the extract is therefore oxidised to IV during paper chromatography. The very simple methods described in this section may not allow of a reliable detection of a Siroset treatment if the fabric has been extracted (dry cleaning) or has undergone wet treatments. Negative tests with the fabric itself or extracts prepared from it should be checked by an analysis of the total hydrolysate [4].

B— ANALYSIS OF THE TOTAL HYDROLYSATE OF EXTRACTED FABRICS

The formation of the combined mixed disulphide (I) in wool is an inherent feature of the Siroset process. Therefore, the most reliable method for the detection of a previous treatment of wool with thioglycollic acid is qualitative paper-chromatographic analysis of a total hydrolysate [4] of the sample extracted with methanol. Fig. 1 shows the spots given by cystine (CySSCy), the mixed disulphide (CySST), and dithiodiglycollic acid (TSST). These compounds are formed during oxidation of a mixture of thioglycollic acid and cysteine by the procedure of Schöberl [5]. Whereas a hydrolysate of untreated wool releases only one compound, cystine, reducing the chloroplatinic acid–potassium iodide reagent, the hydrolysate of a Siroset-treated fabric in addition produced the spot of the mixed disulphide (II). The methanol extract prepared prior to hydrolysis gave the spot of dithiodiglycollic acid (TSST). The method has been applied to many samples of Siroset fabrics and has always given reliable results.

* Abstract of a paper submitted to the Technical Committee, International Wool Textile Organisation Conference, Copenhagen (June 1959).



(i) Oxidation mixture from cysteine and thioglycollic acid
(ii) Total hydrolysate[4] of untreated wool
(iii) Total hydrolysate[4] of a Siroset-treated and extracted fabric (sample A2)
(iv) Methanol extract of A2

FIG. 1—Paper Chromatogram in *n*-Butanol-Acetic Acid-Water (2:1:1) on Schleicher-Schüll Paper No. 2043b, Descending Technique, 24 hr.[5], sprayed with 0·0033 M-$H_2[PtCl_6]$ + 0·0066 M-KI[3]

A peculiar result was obtained on chromatographic analysis of hydrolysates of untreated wool to which dithiodiglycollic acid had been added before or during acid hydrolysis. The chromatogram showed the presence of the mixed disulphide (I), which must have been formed by an acid-catalysed disulphide exchange reaction between wool cystine and dithiodiglycollic acid during hydrolysis. In order to be sure of having found I as the direct reaction product chemically combined in the Siroset-treated proteins, it is necessary to separate uncombined residual thioglycollic acid and its disulphide prior to hydrolysis of the wool sample. This separation was effected by methanol extractions.

A full account of this work will be given in *Melliand Textilberichte*.

Thanks are due to the International Wool Secretariat, Dr. M. Lipson, and Dr. F. G. Lennox for valuable comments on the Copenhagen paper.

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14th October 1959

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Notes

Meetings of Council and Committees
November

Council— 4th
Worshipful Company of Dyers Research Medal— 4th
Pleating Fastness Subcommittee— 6th
Dry Cleaning Subcommittee— 11th
Dyeing Properties of Disperse Dyes— 11th
Diplomas— 17th
Colour Index Editorial Board— 23rd
Publications— 24th
Society of Dyers and Colourists Medals— 25th

The International Federation of Textile Chemists and Colourists
London Congress
15–17–18th September 1959

The Triennial Congress of the International Federation of Textile Chemists and Colourists, the first to be held in the United Kingdom, was organised by the Society of Dyers and Colourists, whose President, Mr. John Boulton, is also President of the Federation. Some 800 visitors from 21 countries took part in the Congress. There was a meeting of the Council of delegates of the I.F.A.T.C.C. at Grosvenor House on the eve of the Congress.

On September 16th, at Church House, Westminster, the President of the Federation, Mr. John Boulton, in his opening address, welcomed the Presidents of the member countries attending and members of the I.F.A.T.C.C. to London and expressed the hope that they would find the Congress as stimulating and enjoyable as the ones which he had previously attended in other cities. He went on to say that the papers to be read covered many of the important developments now taking place in the textile industry. Scientists and technologists were now producing the practical results of the researches into the fundamentals of dyeing and finishing which had gone on in the last 30 years.

J. T. Marsh, the opening speaker, introduced his paper on "Self smoothing fabrics" by referring briefly to the structure of cellulose, stressing the importance of the amorphous region, to the old formaldehyde method for obtaining a crease-resist finish, to thermosetting resins, to reactant resins, to the effect of the different resin finishes on crease-recovery and wet and dry strength of both cotton and rayon fabrics.

W. Schefer spoke on the E.M.P.A. research on "The investigation into the chlorine retention of resin-treated textiles". He outlined the differences between the chlorine retention of the different resin treatments, gave reasons for the increase in chlorine uptake of the different resin-treated fabrics when treated with hypochlorite solutions of varying chlorine content and for the greater decrease in strength between fabrics treated with different resins. Finally he outlined a method of test for determining the retentive capacity of chlorine.

In the afternoon *P. Rochas* presented a paper on "Physico-chemical studies of the effect of carriers on the dyeing of polyester fibres" prepared jointly by himself and M. Courmont. Rate of dyeing curves of various "carriers" were shown, illustrating the increase in the rate of dyeing polyester fibres

and that this depended on the carrier absorbed into the fibre. The effect of carrier on dye uptake was not the same for all dyes, but depended on the solubility and chemical structure of the latter.

H. Zahn was the last speaker of the day. His paper "An investigation of the carbonising of wool" threw some light on an old problem. He gave reasons for the increase in wool fibre damage after carbonising with sulphuric acid. There is an increase in fibre damage on long storage if the wool is not neutralised immediately after carbonising. He showed that, if neutralised immediately after carbonising, there is no appreciable fibre damage and that fibre damage is closely related to alkali solubility.

On the 17th September the lectures were all on modern dyeing techniques. *N. Landquist* spoke of "The recent advances in the application of the Pad–Roll system" developed by himself and his colleagues, C. O. Erikson and B. Mellbin. He stated that the Pad–Roll system was particularly suitable for the application of reactive dyes both of the cold and hot dyeing types, giving reasons for this. Attention was drawn to the necessity of laboratory conditions being closely related to practical conditions if comparative results were to be obtained. Reference was made to work going on in the development of the Pad–Roll system for the application of disperse dyes to silk and man-made fibres.

F. L. J. Lamoen and *H. Borsten* followed with a paper on "A new one-bath method for continuous or Pad–Roll vat dyeing". The disadvantages of the old methods were outlined, the starting point of the new method being evolved from that data. The leuco-potential of vat dyes proved to be of great importance in the investigation, leading to the discovery that if, to a bath containing sodium hydrosulphite and sodium hydroxide, more formaldehyde is added than is necessary for the formation of sodium sulphoxylate, a less negative potential can be obtained at room temperature than by using sodium formaldehyde sulphoxylate only. This was the basis for the new Pad–Roll method. The leuco potential of the vat dyes was used to determine the composition of the reducing bath.

H. R. Hirsbrunner gave the final paper for that day on "Recent developments in the continuous dyeing of wool and its mixtures with synthetic fibres." The work had been done in collaboration with H. Ris, A. Schaeuble, and C. Soiton. Briefly, the process involves the following operations—padding, intermediate drying by dry heat, "Acid-shock" fixing and finally washing to remove the thickening agent. The "Acid-shock" treatment may be replaced partly or completely by steaming under pressure or by a wet heat treatment. It enables the dyer to overcome difficulties in dyeing wool due to wide physical variations and to dye wool and its mixtures continuously in all depths of shade with high fastness properties.

On the final day of the Congress *J. Wegmann* spoke on the "Effect of structure on the change in colour of vat dyes on soaping". He discussed the cause of hue differences which occur on soaping vat dyes and established the fact that a change in colour on developing a vat dye will always occur if the dye after reoxidation is first produced in a metastable form which is stabilised by adsorption on the substrate so that a certain activation energy is required to attain the most stable state of the dye under these conditions.

R. C. Cheetham spoke on "The application of reactive and direct dyes to rayon staple by continuous methods". He stressed the advantages when large weights per colour of rayon staple were to be processed and described two machines eminently suitable for continuous dyeing of loose stock. The system is particularly suitable for the application of reactive dyes. The rate of fixation of direct dyes was important in selecting dyes for mixtures if good results were to be obtained. Much stricter control of conditions was necessary if even dyeing was to be attained with direct dyes than for reactive dyes.

J. B. Robin described the Rhodiaceta process for "The elimination of barriness in the dyeing of continuous filament nylon fabrics with acid and metal-complex dyes". Outlining the theory explaining the dyeing mechanism with anionic dyes, the known physical causes of affinity irregularities are considered and the development of the process which is applicable to all anionic dyes. The process consists in dyeing in a strongly acid bath (pH 3–4), preferably above 100°c., in the presence of a carefully chosen mixture of sulphonated products to control the uptake of dye together with a reducing agent to eliminate any possible oxidation of the fibre.

J. Nüsslein gave a historical review of "The impact of synthetic dyes on the textile industry". He drew attention to the improvement in dyed textiles, to the influence of dye making on other branches of the chemical industry and to the influence of dye research on fibre research and dye application.

The closing paper was by *T. Vickerstaff* on "Reactive dyes for nylon". D. F. Scott assisted in the research. He outlined the way in which this new group of reactive disperse dyes were applied to nylon and then developed by the addition of a mild alkali to the dyebath, the theory of dyeing, the rate of dyeing and fixation and the advantages.

At this juncture a reference to the International Address System should be made. It was a great help to all members since it enabled everyone to hear the lecturer in an easily understood language. This made it possible for questions to be asked and replies given with a speed and ease which would not otherwise have been possible. In fact its use contributed in no small way to the success of the business part of the Congress.

The President said that before he closed the Congress he was sending a message to our Patron, the Duke of Edinburgh. He then thanked everyone who had in any way contributed to the Congress and said that we had been honoured by the presence of the Presidents and Vice-presidents of all our member associations—Professor Elöd, Dr. Ernst, Mr. Zuber, Mr. Sjoklint, Dr. Gribnau, and representing their presidents, Dr. Martina and Dr. Reali.

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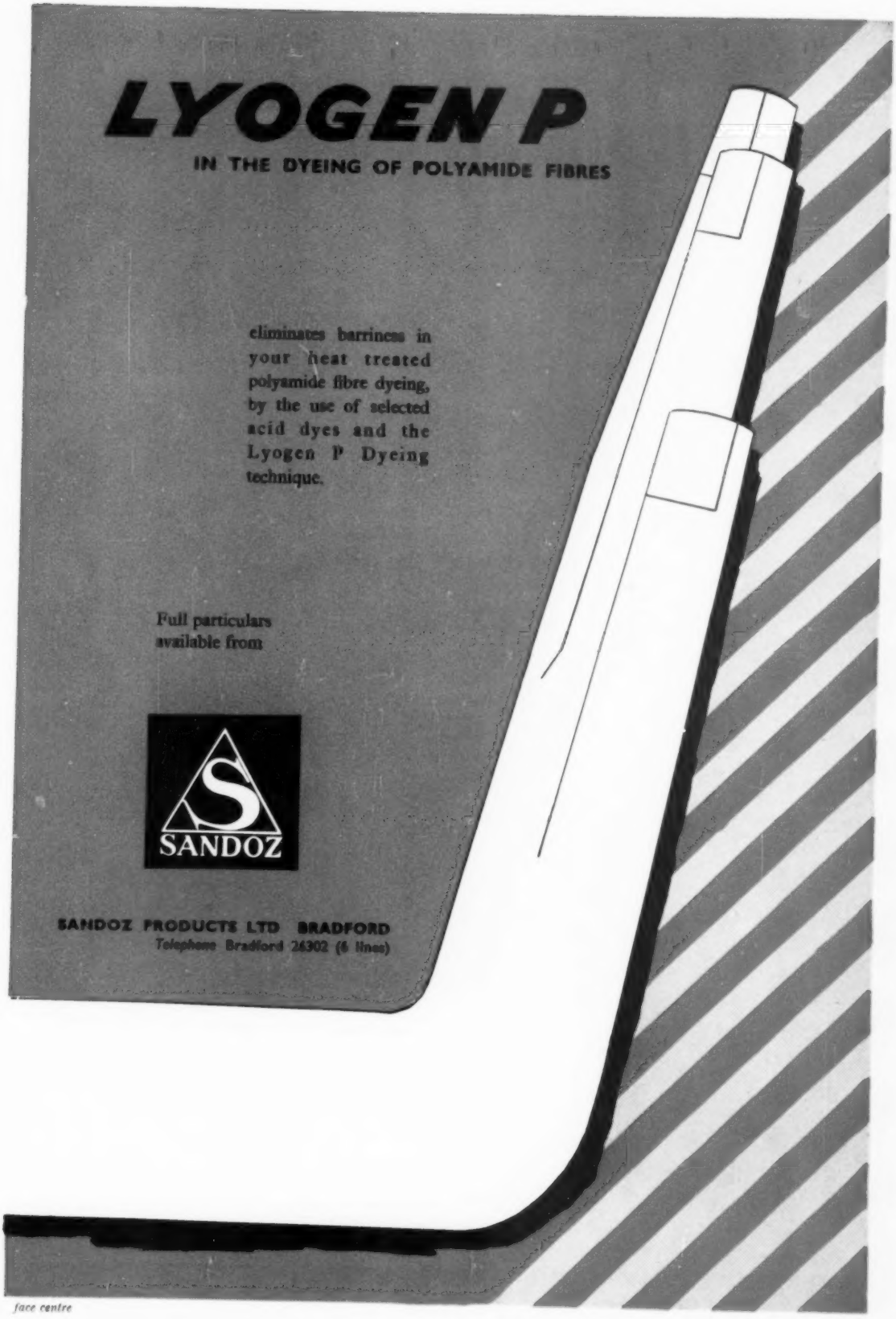

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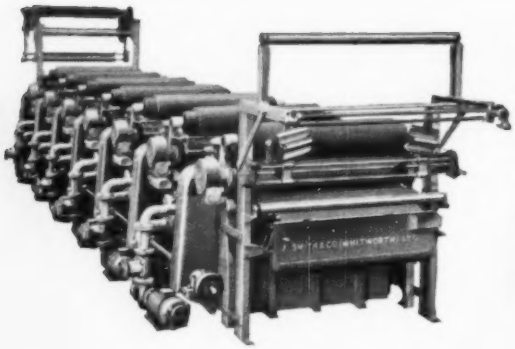

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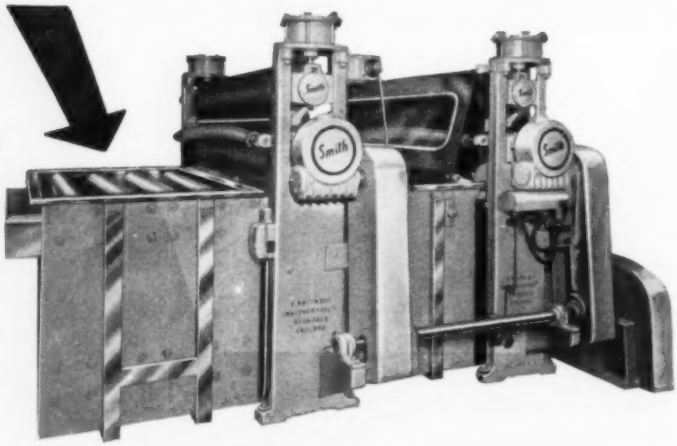

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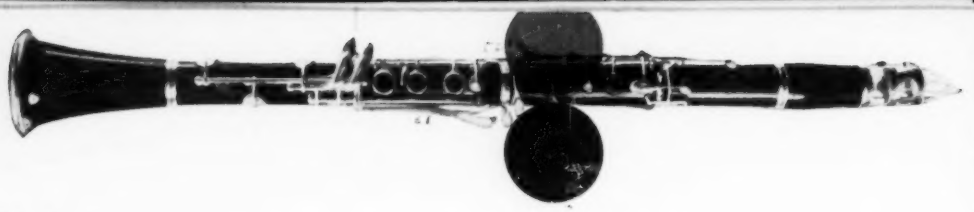

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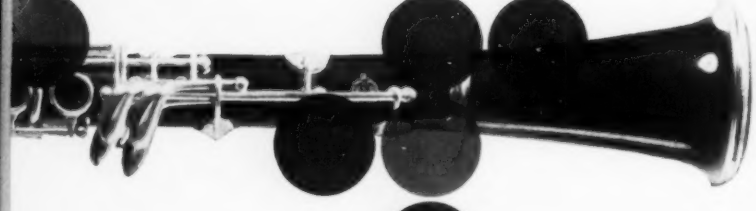

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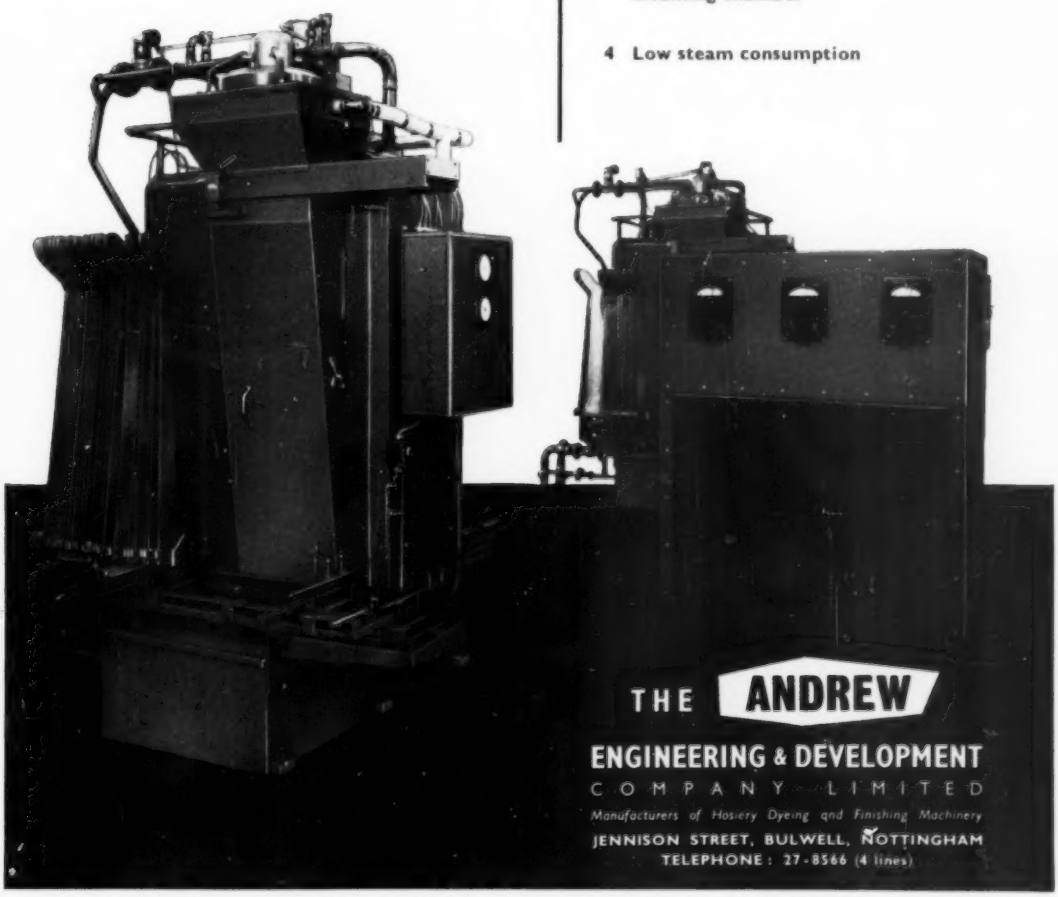

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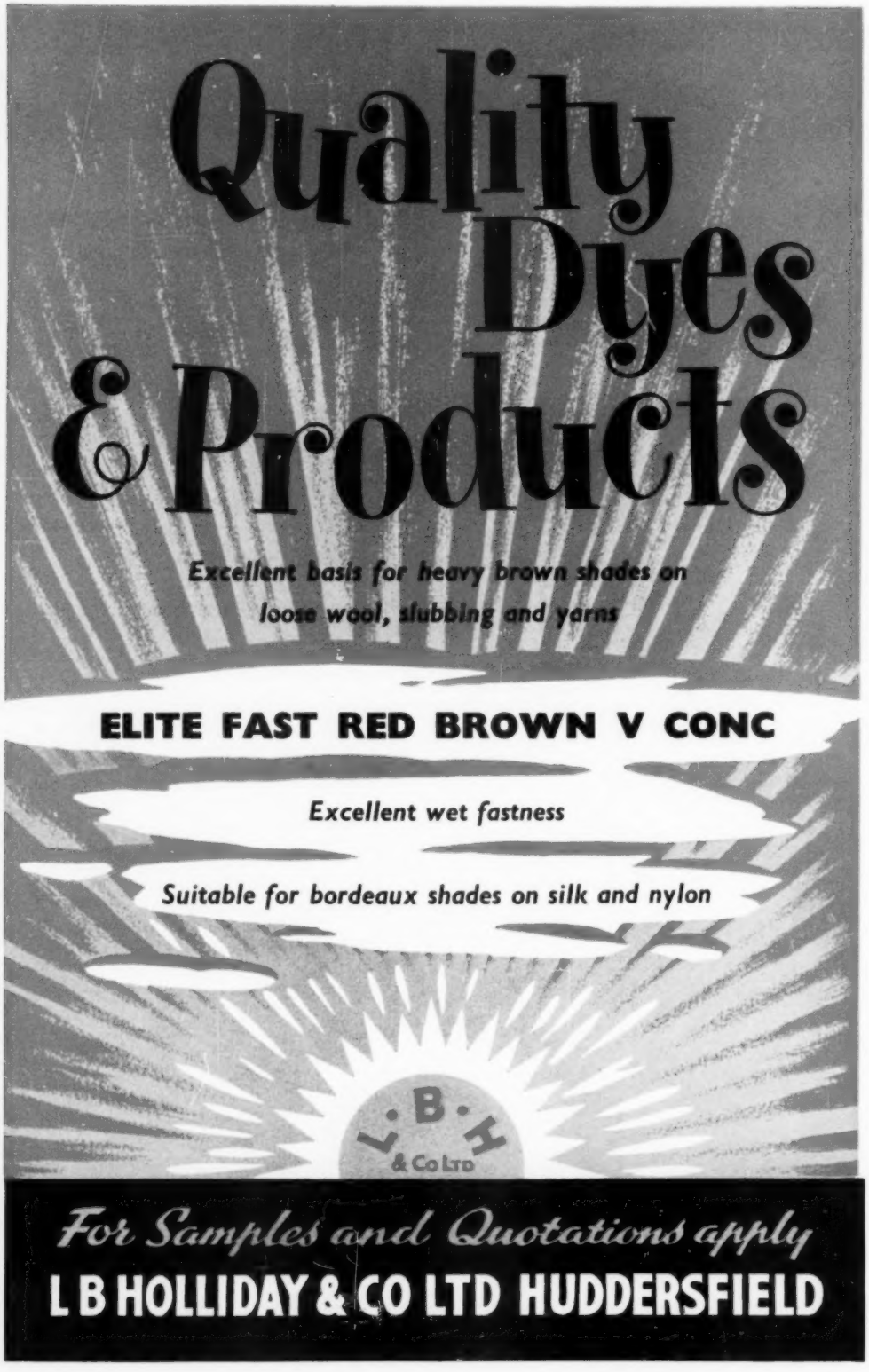
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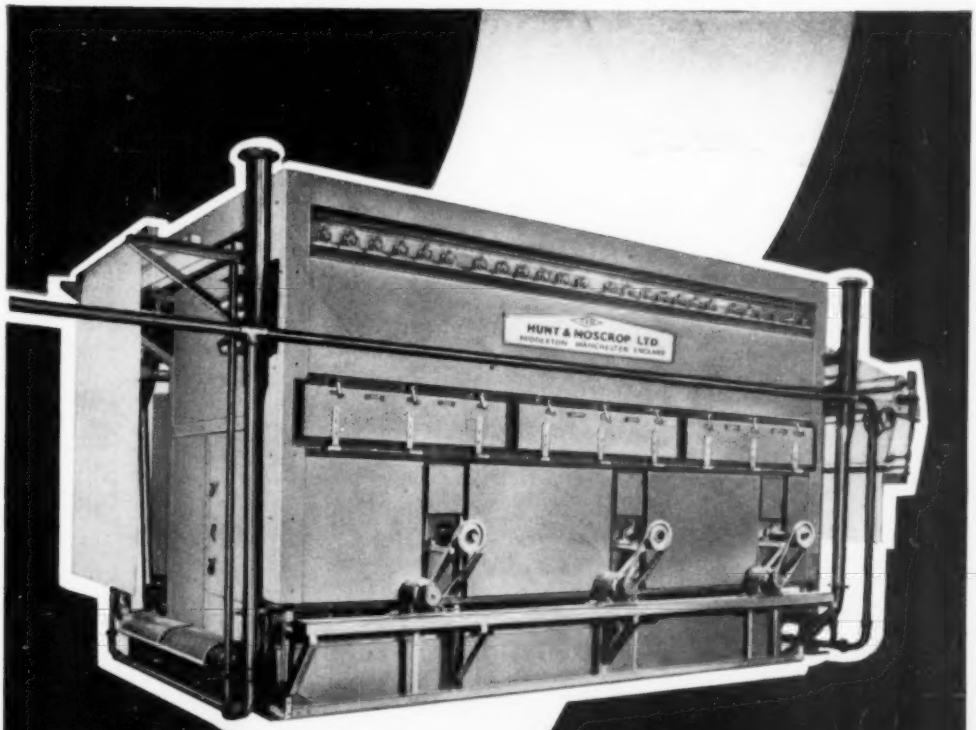

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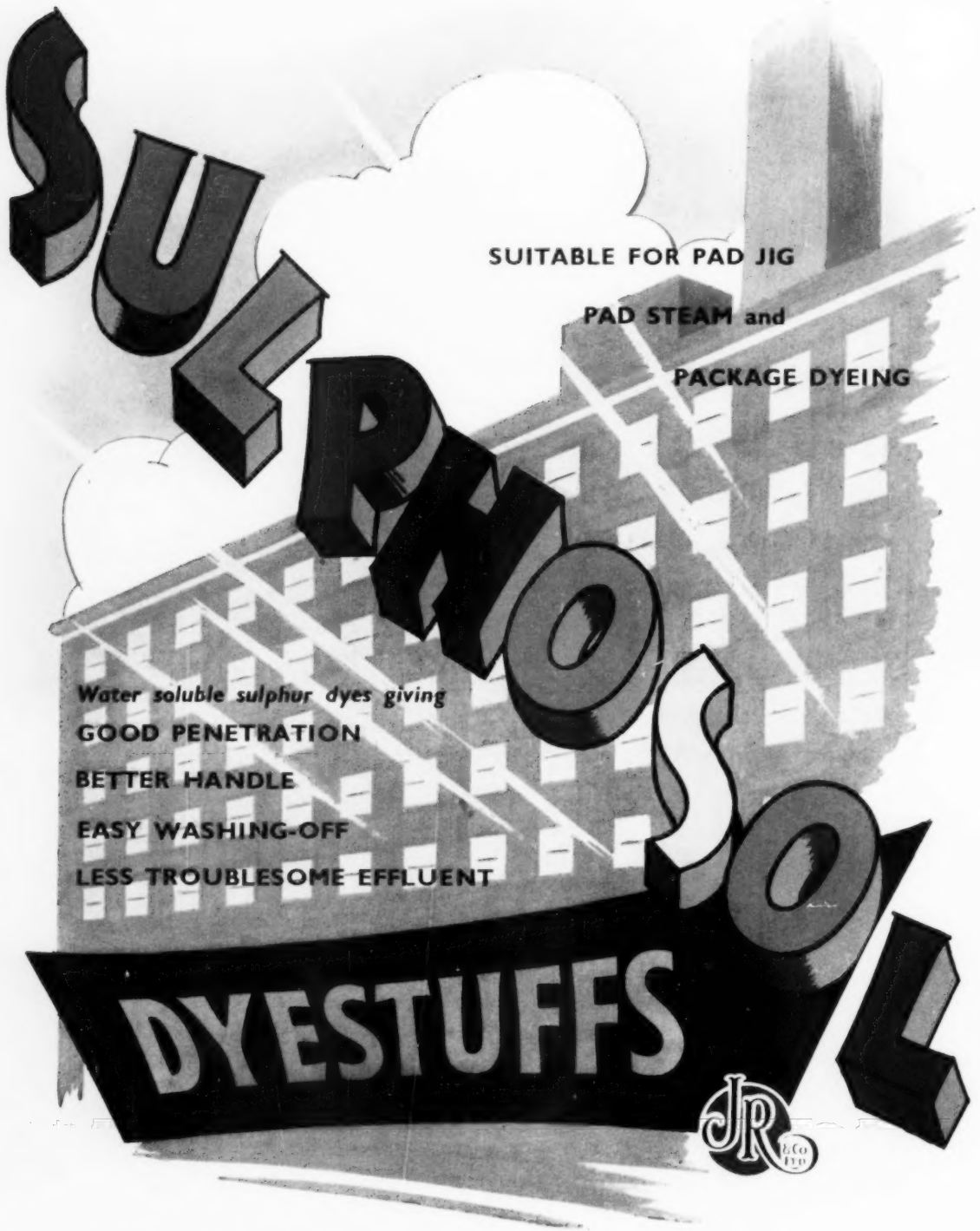

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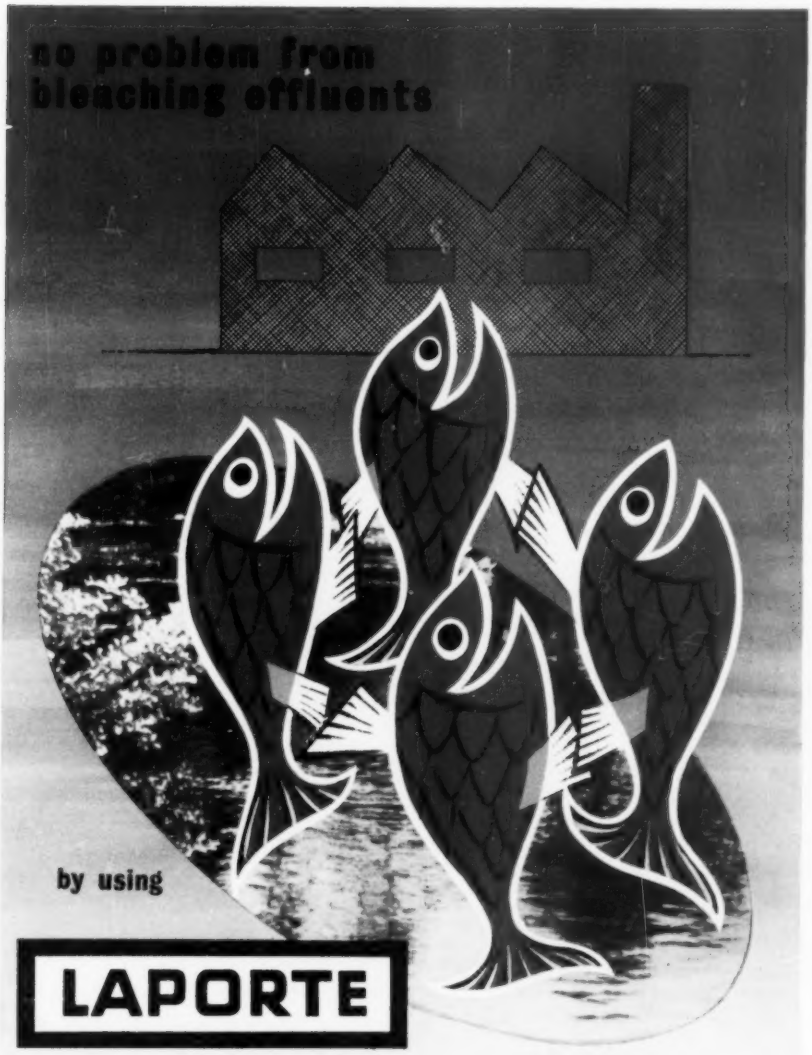

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The next Congress would be in Amsterdam in 1962.

The social side of the Congress was not neglected. A programme of excursions had been arranged to show our overseas visitors and our fellow countrymen some of the places which were typically British. On the Thursday about 130 members went to Stratford-on-Avon and enjoyed a fine performance of *Othello* at the Memorial Theatre. A second party of about the same number visited Windsor Castle and afterwards dined at the Hotel de Paris at Bray. Other excursions were to Hampton Court Palace, Greenwich and the Royal Naval College Museum as well as a sightseeing tour of the City of London.

On Wednesday the lecturers and Presidents with some other officials were entertained to lunch by the Dyers Company. On Friday the Scientific committee entertained the lecturers and their ladies to lunch.

On the first evening of the Congress there was a reception at Guildhall which was attended by most of the delegates and their ladies, who were received by the President and Mrs. Boulton, and was attended by the Lord Mayor and Sheriffs of the City of London. The band of the Coldstream Guards performed during the evening and there was dancing in the Livery Hall to the dance band of the same regiment. This function afforded members attending the Congress an opportunity of meeting and talking with one another, an essential part of any successful congress.

The Congress ended with a banquet on the 18th at Grosvenor House. The guest of honour was Professor Sir Solly Zuckermann, a noted scientist, who proposed the toast to the International Federation of Textile Chemists and Colourists. The President, Mr. John Boulton, responded. Dr. Heinrich Ris proposed "The Society of Dyers and Colourists" to which Mr. Clifford Paine responded.

It was indeed a pleasure to all members of the organising committee to see the large number of members who attended the meetings at Church House; to see their wives and friends so wholeheartedly enjoying themselves and to hear from so many of our overseas visitors how much they had enjoyed the Congress.

ESMÉE SMITH

Use of Fluorescent Brightening Agents in the U.S.A.

The U.S. Tariff Commission report that in 1958 2·9 million lb. of fluorescent brightening agents were sold in the U.S.A. of which 62% was used in detergents, 24% in the paper industry and 12% in the textile industry, the remaining 2% being used in the plastics industry and for miscellaneous purposes.

New Books and Publications

Methoden der Organischen Chemie
(Houben–Weyl)
Band I/2
Allgemeine Laboratoriumspraxis
Teil 2

Edited by Eugen Müller. 4th edition 1959. Pp. xlviii + 1017 + frontispiece + 2 folding tables, Stuttgart: Georg Thieme Verlag. Price, DM 196.00.

Part I of the treatment of general laboratory practice for the 4th edition has already been reviewed (cf. this *Journal* **74**, 427 (1958)), and Part 2, now just to hand, completes it with a survey of general analytical methods. These are prefaced by detailed descriptions (186 pages) of processes, and of their relevant apparatus and machinery, for the pulverisation, separation, and dispersion of materials, which include grinding, sieving, and sifting (by flow, sedimentation, and electrical techniques), methods for the determination of grain fineness, mixing operations for gases, liquids, powders, and plastic substances, emulsification and emulsifiers, and a variety of foam problems including prevention and removal by chemical and physical devices. It is emphasised that for many chemical reactions in heterogeneous phase, the state of diversion of the reactants is a basic factor on which may depend solubility and reaction velocity, efficiency of catalysts and adsorption materials, and the deleterious effects of impurities; while grain size can be of vital influence on properties, e.g. for pigments, it may determine covering power, transparency, and quality of colour. Theoretical treatment is supplied wherever necessary, e.g. the theory of emulsions, and international lists of firms are appended which can furnish the various machines and apparatus described.

In the main chapter on *General Laboratory Methods*, all those operations and processes appear which can belong to the daily routine of the organic chemist. These, which have been enormously increased in number and complexity since the 3rd edition of Houben–Weyl, now include many syntheses with organo-metallic compounds which have been rendered possible by working with exclusion of oxygen and atmospheric moisture, reactions under pressure which have been enabled by special autoclaves, and a great extension in vacuum technique. The various subjects are treated under the subsection headings: *Feed of Liquids* (including conveying and pumping); *Preparation*, *Purification*, *Drying*, and *Storage of Gases* (with the most recent processes for impurity removal, e.g. a universal copper catalyst is described which is specially suitable for the removal of hydrogen, oxygen, carbon monoxide, sulphur compounds, acetylene, etc.); *Gaseous Flow*; *Processes in Liquefied Gases* (ammonia, sulphur dioxide, and hydrogen fluoride); *Processes with Exclusion of Oxygen and Moisture; Explosives and their Manipulation; Micro-operations* (with a comprehensive description of the special apparatus involved); *Reactions under Pressure; Vacuum Production and Control; Heating and Cooling, with Measurement, Registration, and Regulation of*

Temperature (including types of thermometer and thermostat). Each of these sections is provided with its own special bibliography, while the whole volume is rendered especially attractive by 680 illustrations.

The third chapter deals with the chemicals usually found in the laboratory. It contains: a discussion, with definition, of *Purity*; methods for drying solvents; a very large section on the purification and properties of solvents together with tables of their more important constants; a survey of technical solvents; tests for inorganic solvents; and methods for solubility determination. A separate section considers drying agents themselves with their chemical and physical effects.

The fourth and final chapter deals with laboratory hazards and precautions for their prevention, or for the remedial measures to be undertaken when the damage has occurred. These are treated under the headings of mechanical, fire explosion, toxic, electrical, and radioactive hazards. A table listing over 200 dangerous substances with their toxic effects and relevant first aid directions is included. A final section refers to carcinogenic substances.

All the praise accorded in the review of Part I (*loc. cit.*) is also merited by this volume, whose magnitude may be visualised from its author index of 31 pages of names in three columns, and subject index of 44 double-column sides. A more useful volume for the chemist cannot be imagined.

H. H. Hodgson

Symposium on Colour Tolerance, London 1958

The Physical Society Colour Group (*Die Farbe*, **7**, 193–255 (Nov. 1958)). Göttingen, Germany: Musterschmidt-Verlag. Price, 30s. 0d. (In English.)

While practical interest in colour tolerance has been part and parcel of the dyer's trade since it began, only in the last 25 years has colour theory paved the way for the expression of tolerance limits in the form of mathematical specifications in uniform colour spaces. Progress in relating the practical visual estimations to these mathematical specifications has been delayed by the lack of suitable colour measuring instruments capable of a greater colour discrimination than the eye. In the last few years that difficulty has been overcome and the symposium indicates where progress has been made in this country and where difficulties still lie. Perhaps most important, the diverse field of application in which there is interest in instrumental specification of colour tolerance is well illustrated, papers being presented by representatives of lighting, paint, leather, paper, architectural, photographic, printing inks, and textile industries.

Perry's paper covering a survey of colour tolerance formulae shows that there is considerable confusion in the conception of the ideal formula and this disagreement is exemplified in the succeeding papers which have made use of a number of the different uniform chromaticity systems in presenting their data. Strange has emphasised one of the present difficulties in interpreting the magnitude of a "minimum perceptible colour difference" which for four different uniform colour difference formulae, for example, varies in the ratio of 4:5:10:50. In addition there is considerable disagreement as to the relative emphasis which should be placed on chromaticity differences as compared with luminance differences. Hughes and Lott in setting out criteria for the development of instrumental colour tolerance point out that tolerances should be based on visual assessment. Here lies one of the greatest problems; that of relating the practical everyday colourist terms of strength, brightness, and hue used in assessing visual differences to instrumental differences. Thus, while none of the existing formula can be considered universally applicable, it is possible by the selection of suitable constants for the various formulae, to obtain a satisfactory result with practical data for a particular field of application, the variation in the tolerance limit being dependent on differences between instruments and observers' preferences and prejudices in the particular end use.

Mudd has accumulated data in the leather finishing field which has convinced him that at least ten observers as against one instrument are required to assess accurately a small colour difference. While this may not be true in all cases, it does give some indication of the saving which might arise from the development of a suitable instrumental control technique. This economic aspect may stimulate some interest in this field and these proceedings will serve admirably as an introduction with its breadth of information on the various aspects both theoretical and practical which are important in instrumental colour control.

D. Tough

Principles of Biological Microtechnique

A Study of Fixation and Dyeing

By John R. Baker. 1958. Pp. 357. London: Methuen & Co. Ltd. (New York: John Wiley & Sons Inc.). Price, 45s. 0d.

This book is addressed to research-workers, teachers, and students in the fields of pathology, histology, cytology, zoology, and botany. It is concerned with the characterisation and identification of natural objects, such as cells and tissues, and the method adopted is coloration. The biologist is not in the happy position of the dyer, who can use his textile material without much further thought, but he must first stabilise his tissues or cells against enzymatic changes, distortion through drying, and other irreversible effects. This is well described in the first 151 pp. of this volume.

There follows a section of 157 pp. entitled *Dyeing*. It includes an elementary account of the chemical composition and classification of the kind of dyes used in biological staining, a discussion of the mode of attachment of dyes to tissues, and the differential coloration of the component parts of a biological structure. Basic dyes of the triarylmethane and azine groups give different hues on different substrates (*Metachromasy*, 19 pp.), a phenomenon which is encountered also by the wool dyer, though with a wider scope. Special dyes are

used in medical practice for the differential colouring of blood-smears. They are important for the diagnosis of disease and are dealt with in a separate chapter of 11 pp.

Cells and tissues are most easily dyed when dead, but "vital colouring" offers the prospects of colouring living tissues. It is discussed in two chapters (21 pp.).

The volume concludes with a short experimental section on fixation and the properties of dyes. There is a useful list of 559 references and a subject-index. Special mention should be made of a quotation (p. 187) which may bring comfort to the harassed dyer—

> The method of staining, once having taken root in the animal histologist, grew and grew, till to be an histologist became practically synonymous with being a dyer, with this difference, that the professional dyer knew what he was about, while the histologist with few exceptions did not know, nor does he to the present day.

W. BRADLEY

Anfang und frühe Entwicklung des Zeugdrucks in der Schweiz unter besonderer Berücksichtigung des Kantons Glarus

By U. F. Blumer, Pp. 53. St. Gallen: Verlag Zollikofer & Co. A.G. [n.d.]. Price, Swiss francs, 6.25.

The Swiss have devoted considerable time and effort to the study of their economic history, and this short monograph is an interesting account of what has been their most important textile industry. It well illustrates their justifiable pride in a great trade created almost entirely by technical skill and commercial enterprise rather than through wide trading connections, great natural resources, or a large domestic market.

The picture is one of comparable growth to the rest of Europe, the impetus of trade with the Orient and Africa leading to local development, undertaken in the earlier stages with the aid of Huguenot refugees. However, the welcome given to these foreigners was by no means uniformly good. It is interesting to look back on a period from the later seventeenth century until well into the nineteenth, when calico printing (including, nevertheless, some other textile materials) could be regarded with the enthusiasm nowadays reserved for trade in electronics or aircraft.

In its early growth, the Swiss industry escaped many of the economic restrictions which bedevilled our own industry, and even more so that of France. Nevertheless, it had its troubles, especially during the Napoleonic régime, although that period also gave it considerable protection during the periods of blockade. After confederation in 1815, the already partially integrated system of printing and merchanting which had grown up, with branches at many of the leading ports of the Mediterranean, not to speak of personal attendance at the greatly important fairs of the time, enabled a great extension of trade to take place until the 1890s. By then free trade was appearing to be almost an anachronism, forcing the Swiss industry into wider fields, only to meet British and Alsatian or Dutch competition on an ever increasing scale. However, there still remained an export market for high-class hand-printed materials for Africa and elsewhere. The silk industry was, and remains, an independent development in the eighteenth and nineteenth centuries, even if calico has been replaced by silk and rayon in some instances.

The canton of Glarus is of greatest interest, as it was in this district that textile printing reached its greatest size in the nineteenth century, and at the peak was turning out two-thirds or more of the total Swiss production. Nevertheless, it had gone severely into decline even before the First World War, and retained only its specialised finishing or hand-printed styles on any scale. The growth of Glarus was similar to that of Lancashire in that printing was superimposed on an existing cottage spinning and weaving industry. However, it could never overcome the disadvantages of its geographical location, and the absence of fuel and of a marketing centre such as Manchester. The textile industry is, of course, by now a secondary industry throughout Switzerland, retaining its position almost solely on the traditional skills of its people. In its day Glarus, not to speak of other cantons, contributed greatly to the foundation of textile industries in Portugal, Russia, Germany, France, and Italy.

J. W. REIDY

Manufacturers' Publications and Pattern Cards

The Society does not accept any responsibility with regard to the statements in the following notes. Any publication abstracted may be referred to by members of the Society on application to Dr. C. B. Stevens, Dyeing Department, Leeds University

Ciba Ltd.

THE NEW MICROFIX DYEING PROCESS— This card contains pad-dyeings on cotton of 11 Microfix pigments, including two new members, Yellow 5GN and Rubine BN. Application has been greatly simplified by the introduction of a single binder Microfix Binder 59, enabling two additional binders and sodium alginate and ammonia to be omitted in the preparation of the padding liquor. A softer handle is obtained and additional softners added to the padding liquor are much more effective in the new formulations.

CIBACET BRILLIANT VIOLET 3B— This disperse dye gives bluish violets on polyester fibres and Acrilan and bright reddish violets on secondary cellulose acetate and triacetate. It builds up well and is level dyeing and dyeings have good fastness to light, wet treatments, and sublimation. It is also of interest for direct printing on these fibres but is of no interest for dyeing or printing other polyacrylonitrile fibres or polyamides. Fastness figures on secondary cellulose acetate include— Light (daylight) 7 (bright material), sublimation 4–5, washing SNV a 3–4.

CIBACET YELLOW GWL— This disperse dye gives reddish yellows when dyed or direct printed on secondary cellulose acetate, triacetate, polyester fibres, and Acrilan. It is very suitable for use in mixtures, and dyeings on secondary acetate are dischargeable to white. Fastness figures on secondary acetate include— Light (daylight) 7 (bright material), perspiration SNV 4, washing SNV a 4–5.

CIBACRON BRILLIANT BLUE BR: CIBACRON VIOLET 2R— This card describes the printing application and properties of these two reactive dyes on cellulosic fibres. Brilliant Blue BR may be used alone or alongside dyes of other classes which are not fixed in acid steam and can also be printed on naphthol prepares and used for coloured resists under aniline black, naphthol blue, and solubilised vat dyes. Violet 2R is particularly suitable for use in mixtures. It is not suitable for coloured resists.

Farbwerke Hoechst A.G.

FAST COLOUR SALT PRINTS ON NAPHTOL AS IMPREGNATIONS— This loose-leaf card contains 84 prints in two depths on cotton cloth of a wide range of Fast Colour Salts printed on Naphtol AS, AS–D, AS–BS, and AS–G grounds. The text includes suitable printing recipes, data on the stability of the print pastes, and notes on the selection of suitable coupling and diazo components. Fifteen examples of commercial printings are included, produced with azoic combinations and solubilised vat dyes printed alongside them.

REMAZOL GOLDEN YELLOW G; BRILLIANT ORANGE RR; RED 3B; BRILLIANT VIOLET 5R— These new members of the Remazol range of reactive dyes for cellulosic fibres are very similar in dyeing and printing behaviour and in fastness characteristics to the first members of the range and extend its scope considerably. Fastness characteristics on cotton include—

	Light	Washing 75°c.	Perspiration
Golden Yellow G	6	5	5
Brilliant Orange 2R	5–6	4–5	5
Red 3B	7	4–5	5
Brilliant Violet 5R	6–7	4–5	4–5

Imperial Chemical Industries Ltd.

DIRECT DYES FOR STAPLE VISCOSE RAYON— This card contains dyeings on bright spun viscose rayon cloth of 55 direct dyes from the Chlorazol and Durazol ranges and 12 Chlorazol Liazo dyes, including "CR" quality types where available. The sixteen pages of text and the data appended to each set of dyeings provides all the necessary information on the application, dyeing behaviour, and fastness properties of the dyes which have been selected for their suitability for the dress goods trade. It is noted that some are available in highly concentrated form ("P" brands) and these are preferred where a padding technique is to be used. Dyeing behaviour is classified according to the S.D.C. recommendations, and additional information is given for the effect of temperature and salt concentration on dyebath exhaustion (illustrated graphically) and rate of dyeing and levelling. It is noted that the indiscriminate use of metal-sequestering agents should be avoided when dyeing those dyes containing copper in the molecule, that several of the yellows can cause accelerated fading of certain other dyes, particularly violets and blues, and that treatment of the dyeings with Silicone M475 in no case has any effect on hue and light fastness.

TECHNICAL INFORMATION LEAFLETS

Dyehouse No. 476. Dyeing of Wool/Viscose Rayon Carpet Yarns— The Durazol Union dyes, supplemented by selected Chlorazol Union and Chlorazol dyes, provide the most economical means of producing a wide range of colours of good fastness to light and wet treatments on wool/viscose rayon carpet yarn. It is preferable to select a dye giving as far as possible the colour required and then modify this as necessary, e.g. using Durazol Union Brown B shaded with Union Orange Y and Union Grey B. Notes are given on control of dyebath pH, dyeing temperature, and dyebath additions together with data for fastness to light, water, and sea water.

Dyehouse No. 490 (Replaces No. 399). Vulcaprene A: Applications in the Leather Industry— Vulcaprene A is a polyesteramide type synthetic rubber containing in its molecule certain chemical groups similar to those occurring in proteins. It is thus compatible with leather and this leaflet describes its use as (1) a finish and (2) an adhesive in the leather trade.

Dyehouse No. 491. Use of Procion Dyes for Dyeing Wool/Cellulosic Fibre Blends— The cold dyeing Procion dyes may be used to give a wide range of bright colours, including contrast effects, on wool/cellulosic mixtures, the fastness obtained being much better than that given by acid and direct dyes. Using the normal cold-dyeing technique as for cellulosic fibres, the cellulosic portion is dyed and the wool only slightly stained. The greater the degree of modification undergone by the wool before dyeing, e.g. in reclamation or due to chlorination, the greater the uptake of the Procion dye. The recommended procedure is to dye the cellulose first using trisodium phosphate for wool/cotton and soda ash for wool/viscose. A "soaping-off" after dyeing is essential but this may also be used to "fill in" the wool using selected neutral-dyeing acid dyes.

Dyehouse No. 492. Abnormal Fading Behaviour of Vat Yellow and Vat Green Mixtures, with special Reference to Caledon Yellow 4GL— It has been found that when the fast-to-light Caledon Yellow 4GL is used with Caledon Jade Green XBN and Green 7G to produce yellow-greens it promotes catalytic fading of these dyes and the light fastness is significantly reduced. Using the "S" brand, mixtures of Yellow 4GL with Jade Green XBN in the ratio of 2:1 and with Green 7G in the ratio of 1:1 represent the upper limit of yellow for high light fastness. With Olive Green B the ratio is 1:1 and with Jade Greens 2G (or 4G) marked catalytic fading occurs over the range 1:2 to 4:1 so that this latter combination is not recommended.

Dyehouse No. 494. Procion Dyes for Garment Dyeing— Cold dyeing Procion dyes may be used by the garment dyer for producing bright, pale to medium depth dyeings on bed-linen, towels, curtains and the like, with a fastness to light and wet treatments approaching that given by vat and azoic dyes, the use of which is now favoured. Careful preparation of the material before dyeing is necessary, it being particularly important that all traces of chlorine or oxidising agents be removed prior to dyeing, as well as resins, and that the goods be neutral before entering the dyebath.

Dyehouse No. 495. Fastness to Hypochlorite Bleaching— The I.S.O. method for determining fastness to hypochlorite bleaching specifies that this should be determined at pH 11. While the majority of dyes used on yarns are not sensitive to pH differences during bleaching a few are more affected at lower pH values. This leaflet gives figures for the fastness to hypochlorite bleaching of the full range of vat dyes, 5 Procions, 2 Alcian "X" dyes, and a range of azoic combinations, tested at pH 9 as well as pH 11.

Dyehouse No. 496. Weathering Fastness— Azoic Dyestuffs— For azoic combinations, the method of assessing fastness to weathering has been extended by exposing the dyed patterns under two kinds of conditions at Wilmslow, Cheshire, between April and October 1958, and Bombay, India, between November and February 1958, which are considered to represent the extremes likely to occur anywhere in the world. The results are given in this leaflet.

Dyehouse No. 497. Application of Vat and Azoic Dyes to Wool/Cellulosic Fibre Blends— For certain deep dyeings on such unions where high wet fastness is required the cold-dyeing Procion dyes (see T.I. Dyehouse No. 491) are not very suitable. It has been found that selected vat and azoic combinations may be applied using a maximum concentration of 4 parts caustic soda flake per 1000 parts liquor at a maximum temperature of 40°c., these conditions having been shown to produce no more reduction in tensile strength and abrasion than may be tolerated in most instances. Details of the recommended dyes and dyeing methods are given.

Dyehouse No. 498. Procion Brilliant Blue H7G: Dyeing of Cellulosic Fibre by Batchwise and Pad–Roll Procedures— Dyeings of higher tinctorial strength and greater reproducibility are obtained with this dye on viscose rayon when using batchwise processes if trisodium phosphate is replaced by a 4:1 mixture of soda ash and sodium carbonate. No change in the recommendations for cotton is made. When using the pad-roll method for viscose rayon either a reduction in the amount of soda ash or its replacement by caustic soda is advised. With cotton the replacement of soda ash by caustic soda is recommended.

Dyehouse No. 499. Wash and Wear Finishes based on Calaroc EU— Application methods and formulations are given for using this product for a variety of finishes on cotton and viscose rayon staple fibre cloths.

Dyehouse No. 501. Use of "V"-Brand Pigment Pastes in Leather Finishing— The "V"-brand pigment pastes may be used in exactly the same way as the water-soluble Neran Brilliant dyes in aniline-type finishes and water-pigment finishes where increased fastness to light and rubbing is required.

Dyehouse No. 502. The Dyeing of Wool/Cellulosic Fibre Unions under Acid Dyebath Conditions— A single-bath method is described for dyeing particular types of wool/cellulosic fibre mixtures, e.g. wool or wool/mohair pile fabrics using mixtures of acid and direct dyes under acid dyebath conditions instead of the more usual neutral conditions, thereby giving a more resilient pile. Excessive staining of the wool is prevented by adding Taminol WR and Dispersol AC.

Dyehouse No. 504. Lissapol GLN in the "Poensgen Contra-flow Carousil" Washing Machine.

Dyehouse No. 505. Wool/Natural Silk Blends: Dyeing of Blended Piece Goods— Methods are outlined for producing solid and two-tone effects and reserve effects on the silk. Cold-dyeing Procion dyes offer a very controllable method of dyeing such materials since, using the cold-dyeing batchwise technique, the wool is practically unstained, unless it has previously been severely damaged. It may then be dyed under such conditions that staining of the silk is kept to a minimum.

Dyehouse No. 506. Printing of "Orlon" (Type 42), "Courtelle", "Acrilan", and "Dralon" Acrylic Fibres— The information accumulated to date on the printing of these acrylic fibres with vat, disperse and Alcian "X" dyes is presented together with that for selected acid dyes on Acrilan only. Results so far suggest that the behaviour of Dralon in printing is similar to that of Courtelle. Fastness data are appended.

Dyehouse No. 507. Soledon Dyes: Application to Wool— Poor levelling and penetration and a tendency to give skittery dyeings generally restricts the use of the solubilised vat dyes to loose wool and slubbing and even then only a selection of dyes of this type are of interest as the remainder are difficult to develop into the parent vat dye in presence of wool. Four methods of dyeing are described and the Soledon dyes recommended for use on wool are listed, together with the preferred dyeing method and fastness data.

Dyehouse No. 508. Procinyl Dyes for the Printing of Nylon and other Synthetic Fibres— The Procinyl range of reactive disperse dyes are particularly suitable for producing prints of high wet fastness on polyamide fibres. Nafka Crystal Gum Supra gives level prints, good definition, and high colour yield. During wet processing, Procinyl-printed goods may be piled wet without danger of marking-off on to adjacent material. They are also of interest on secondary cellulose acetate and triacetate giving prints of generally higher wet fastness than are obtained with conventional disperse dyes and of excellent fastness to heat treatments on triacetate. Except for Procinyl Yellow G, they are of little interest on Terylene and none are of interest on wool, silk, acrylic fibres or Terylene/cellulosic fibre blends. All, except Procinyl Blue R, are dischargeable to white on nylon, acetate, and triacetate.

Dyehouse No. 509. Calatac VB in Nylon Hose Processing.

Dyehouse No. 510. Procion Dyestuffs on Cotton: Effect of Various Resist Treatments— The effects of Permafresh LF (Warwick Chemical Co., U.S.A.), Fixapret CP and 140 (BASF), and Zeset MC (du Pont) resins on the hue and light fastness of Procion dyeings on cotton are tabulated.

Dyehouse No. 511 (Replaces No. 418). Alcian Dyestuffs: Dyeing of Wool/Cellulosic Fibre Unions— Alcian Blues 8GX, 5GX, 2GX and Greens 2GX and 3BX can be applied to wool/cellulosic fibre mixtures using a two-stage process in which the cellulosic fibre is first dyed with the Alcian dye from an acetic acid bath at the boil, adding Lissolamine A 50% as a restraining agent as required. Deep dyeings are "soaped" by adding Lissapol ND to the alkaline development bath after development has been judged complete. The wool portion of the well-rinsed pattern is then dyed in a fresh bath with suitable dyes, Coomassie Turquoise Blue 3G, alone or in combination with Procion Brilliant Yellow H5E, Carbolan Brilliant Blue 2E, and Coomassie Ultra Sky 8E being particularly recommended. It is important that correct pH conditions are established before applying the wool dye to ensure level dyeing and adequate exhaustion.

Sandoz A.G.

CUPROFIX PRINTING COLOURS ON COTTON AND RAYON— This card contains direct prints in two depths on mercerised cotton sateen and spun viscose rayon cloth of 28 Cuprofix Printing dyes. They give considerably cheaper prints than vat or solubilised vat dyes, particularly when large blotch patterns are used. The recipes are simple and fixation straightforward and reliable. The print pastes are very stable and the printed goods may be stored as long as necessary before fixation and are much less susceptible to variations in steaming conditions than vat dyes. Six examples of roller and screen prints from bulk working are included.

FORON AND SOLAR DYES ON TERYLENE/RAYON BLENDED FABRIC— This card contains 18 dyeings on a 67% Terylene/33% viscose rayon staple mixture cloth of mixtures of Foron disperse dyes (for the polyester fibre) and Solar direct dyes (for the cellulosic fibre). Dyeing is continued for 1 hr. at the boil in presence of Sandozol KB and Dilatin DB as carrier for the disperse dye on the Terylene. All the dyes are also suitable for dyeing $> 100°C$.

PAD-ROLL DYEINGS WITH SOLAR COLOURS ON COTTON AND RAYON— This card contains dyeings in two depths on cotton and spun viscose rayon cloth of 49 Solar direct dyes produced on the Pad-Roll machine, in this instance the padding temperature being 80°C. and the expression 80% and dyeing being continued for 4 hr. at 85°C. (8 hr. for the black). Normally highly concentrated brands are recommended but if the solubility is adequate the standard brands may be used and with the turquoise blues additions of salt are recommended. The solubility of both the standard and concentrated brand of each dye at 80–85°C. is given.

ULTRA-DISPERSED ARTISIL DYES ON ORLON 42 ACRYLIC FIBRE— This card contains dyeings in light and medium depth of 23 disperse dyes on Orlon 42 cloth and two mixture dyeings. The medium depth dyeings are very close to the maximum depth obtainable at 100°C. At temperatures up to 120°C. considerable deeper dyeings are obtainable with dyes which may be dyed at elevated temperatures and 14 of the range are suitable for this purpose.

BRILLIANT ALIZARINE MILLING BLUE F2GL— This acid dye gives bright blues of excellent wet fastness on wool, silk, and polyamide fibres. It is unaffected by chrome in the dyebath and dyeings on wool are unaffected by chlorination. It is also of interest for Vigoureux printing and direct printing on protein and polyamide fibres. Fastness figures on wool include— Light 6, perspiration SNV 4–5, alkaline milling SNV 5.

PALETTE NOS. 1 AND 2— "Palette" is a review devoted to colour and colouring matters and colouring processes. Articles in the first issue include "Light and Colour", "The Psychology of Colours", "The New Textile Fibres", "The Modification of Sulphur Dyes", and "The Assessment of End Use Performance: the Aim of Material Testing". No. 2 includes "The Use of Oligomers in Fundamental Research into Synthetic Fibres", "Colour and Molecular Structure", and the second section of "The Modification of Sulphur Dyes".

Sandoz Products Ltd.

SULFONINE BRILLIANT GREEN 3GL— This acid dye gives bright greens of good fastness to light and wet treatments on wool and polyamide fibres. It is applied from neutral or weakly acid dyebaths, is stable to chrome and is also of interest for medium depth dyeings on wool/nylon mixtures. Fastness figures on wool include— Light 5–6, washing (60°C.) 4–5, alkaline milling 4–5.

Abstracts from British and Foreign Journals and Patents

The titles of abstracts may be modified. Abbreviations of names of firms are listed in J.S.D.C., **68**, *23 (Jan. 1952), and also, together with symbols and the periodicals abstracted, in the annual index*

I— PLANT; MACHINERY; BUILDINGS

Automatic Steering of Thread Correcting Machines

H. Mahlo *Melliand Textilber.*, **40** 661–665 (June 1959)

A clearly illustrated review of devices for compensating waviness and other misalignments in stentering fabric precedes a detailed description of the author's "Orthomat" photo-electric automatic regulating device. This comprises three measuring heads across the fabric, each containing two inclined photo-cells, which respond differently to light passing through the fabric if the weft threads are inclined. After amplification these differences actuate regulators until the photo-cell response is equalised. S.M.J.

High Temperature Dyeing Machines for Packages, Cakes, Loose Material, and Piece Goods

J. Recker *Melliand Textilber.*, **40**, 652–654 (June 1959)

A competent review of recent developments in high temperature dyeing machines, and of the reasons for them. Changes in pumps and circulation systems, heat exchangers, sampling systems, and methods of making additions are described. Future developments towards automation are then discussed. S.M.J.

PATENTS

Washing or Dyeing Machine for Loose Material

Fleissner & Sohn *BP* 821,327

A machine much shorter than the usual loose fibre dyeing machine has a bath with an inlet for the liquor. A horizontal perforated drum rotates either wholly or largely immersed in the liquor. The material to be washed or dyed is fed on to the outer surface of the drum. The liquor is sucked from the bath into the drum so causing the material to be held firmly to the drum without other assistance. Means are provided to remove the material from the drum after it has rotated with the drum through the greater part of a revolution. C.O.C.

Applying Finish Solutions to Rayon Cakes

American Viscose Corpn. *USP* 2,888,363

The cakes, after their final wash, are centrifuged and then treated with a finishing solution which is then extracted from them for use on later batches of cakes. By use of the apparatus described the extracted finishing solution remains undiluted. C.O.C.

Continuous Electrical Heating of Yarns

Heberlein & Co. *BP* 821,146

The yarn passes through a metal tube whose inner surface has a spiral groove within which is an insulated resistance wire. The tube has at both ends coaxial tubular extensions of a material of bad heat conductivity. Both tube and extensions are surrounded by an outer insulating layer. C.O.C.

Uniformly Heating Flexible Strips or Tapes

Svenska Aktiebolaget Gasaccumulator *BP* 820,602

The material is wound together with a flexible heating band on to a roll. During the winding heat is applied to the material from the heating band. At least one pressure roller bears on to the roll during its rotation. The process may be used e.g. for vulcanising neoprene-impregnated nylon tape. C.O.C.

Combined Feeler Clip and Pin Chain Links for Tenters

Famatex *BP* 820,988

Festoon Rods for Use in Dyeing Wallpaper, Textiles or the like

F. B. Austin *BP* 820,910

Wooden rods having metal sleeves where they are engaged by the rod handling mechanism have a longer working life than plain wooden rods. C.O.C.

Multi-nip Calenders

Beloit Iron Works *BP* 818,429

Much greater flexibility of working and improved control of the load forces and their distribution across the calender are obtained if the ends of each roll above the bottom roll are rotatably supported in separate bearings. These bearings are separately adjustable to adjust the position of the supported roll with respect to the adjacent rolls. C.O.C.

Raising Machine

Tomlinsons (Rochdale) *BP* 821,850

A machine in which the amount of raise imparted to the fabric is automatically indicated within very fine limits. C.O.C.

Machine for Applying Transfers to Stockings, etc.

Paramount Textile Machinery Co. *USP* 2,889,648

Deposition of Inks, Paints, and other Viscous Liquids— Multicolour Printing in One Operation

McCorquodale Colour Display *BP* 821,152

A machine for multicolour printing in one operation. It has the advantage that splashing of the ink upon separation of the sheet being printed is avoided. C.O.C.

III— CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

Table of Textile Auxiliary Agents

S. Jost *Textil-Rund.*, **14**, 329–335 (June), 388–396 (July), 448–460 (Aug. 1959)

Variability of Wool Fat. I— Acid Number and Refractive Index

G. Nitschke *Faserforsch. und Textiltech.*, **10**, 380–387 (Aug. 1959)

Methods of determining the acid number and refractive index are discussed and the variations of these quantities from one wool fat to another. The influence of storage on these quantities is examined and changes in wool fat on storage are discussed. W.R.M.

Hydrotropic Effects and their Significance in Textile Finishing

H. Rath and S. Müller *Melliand Textilber.*, **40**, 787–792 (July 1959)

Theoretical considerations and experimental findings lead to explanation of the solubilising properties of carbonyl containing hydrotropic substances in terms of both dipole forces and hydrogen bonds. Practical results further illustrate application of the system cyclohexanol–cresol–sodium hydroxide in mercerisation, and the dispersion of dye aggregates, accompanied by some accretion of hydrotropic agent on the smallest particles. S.M.J.

PATENTS

Polyalkylene–Polyamine Condensates as Textile Assistants

Boehme Fettchemie *BP* 821,082

Textile assistants, soluble or dispersible in water, are obtained by condensing polyalkylene–polyamines for up to 30 min. at < 100°C. with esters of aliphatic carboxylic acids of 6–18 C followed by making the reaction mixture weakly acid with a low-mol.wt. carboxylic acid of 1–5 C. Thus hardened castor oil (200 g.) is treated at 75°C. with ethylene diamine (30 g.). The mixture is stirred at 75°C. for 10 min. and then with addition of an emulsifying agent. (condensate of 5 mol. ethylene oxide with 1 mol. stearic acid) (10 g.) is stirred into 3% acetic acid (760 c.c.). Perlon treated with 0·3% solution of this condensate, centrifuged to a moisture content of 40% and then dried at 60°C. has a supple smooth handle and antistatic properties. C.O.C.

Flame-resisting Finishes

Albright & Wilson *BP* 821,503

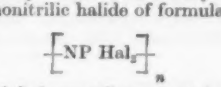
The flame-resisting property of the nitrile methylol-phosphorus polymers described in *BP* 761,985, 740,269, and 764,313 (J.S.D.C., **73**, 61 (1957); **72**, 40 (1956); **73**, 216 (1957)) is increased by mixing the polymers with a non-volatile bromine derivative, e.g. a 2,3-dibromopropyl ester of a phosphonitrilic chloride of the type described in *USP* 2,681,295 (J.S.D.C., **71**, 483 (1955)).

BP 821,504

The material is impregnated with an aqueous emulsion formed by agitation from (*a*) a water-soluble fibre-penetrating resin-forming intermediate capable of reacting with (*c*) to form a nitrogenous, phosphorus-containing thermosetting resin, (*b*) an inert water-immiscible organic liquid, (*c*) an emulsifying agent, (*d*) enough water to form the continuous phase, and (*e*) a powdered phosphorus-containing thermoset polymer. The impregnated material is baked and then is not only flame-resistant but also has good crease-shedding properties.

BP 821,505

Thermosetting flame-resisting agents are obtained by reacting a terminally-unsaturated alkenyl alcohol neutral ester of a phosphonitrilic halide of formula—



($n > 1$) with a polyhalogenoalkane containing at least two Cl and/or Br atoms attached to the same C atom in presence of a free radical reaction initiator. Thus a neutral allyl ester of a phosphonitrilic halide (16) was emulsified with bromoform (15), $NaHCO_3$ (1·5), and poly(vinyl alcohol) (0·6) in water (70), heated to 80°c., K persulphate (0·6) added and heating continued for 1 hr. at 80–86°c. Cotton cloth impregnated with the resulting emulsion, dried, and baked at 140°c. for 6 min. had excellent flame resistance. C.O.C.

Gas Fume Fading Inhibitors

Rohm & Haas *USP* 2,888,314

Compounds of formula $RNHCH_2CH_2CN$ (R = phenyl, benzyl, cyclohexyl or aliphatic hydrocarbon of > 7 C) e.g. t-octylamino propionitrile, are excellent gas fume fading inhibitors which are fast to drycleaning and washing. They may be applied to the fibre before, after or during dyeing. C.O.C.

Hardenable, Basic Silicon-containing Condensates

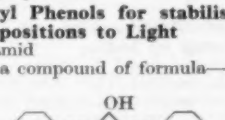
Chemische Fabrik Pfersee *BP* 820,529

Products soluble or dispersible in organic solvents, water or dilute aqueous acids are obtained by heating an aminoplast-forming nitrogen compound, paraformaldehyde, a monocar- -lic acid of 8 C, an oxyalkylamine, and a compound of formula $R^1_nSi(OR^2)_{3-n}[R^1_xSi(OR^2)_{3-x}]_yOR^2$ (R^1 = same or different Alk or Ar; R^2 = same or different, Alk, Ar or acyl; $n = 0, 1, 2$ or 3; $x = 0, 1$ or 2; $y = 0$–6). They are suitable for making into lacquers and coatings and as finishing agents for textiles, paper or leather. Thus paraformaldehyde (1000), melamine (330), and triethanolamine (330) are stirred into methanol (2500). The mixture is brought to 60°c. and a molten mixture of stearic acid (1200) and dimethyl distearoxy silane (600) stirred in. The temperature is raised to 70–75°c. in 75 min. and to 110°c. in 7 hr. The resulting reddish-brown resin is formed into a fine dispersion by heating it with 6% aqueous acetic acid. This dispersion is diluted to contain 50 g. of resin and 5 g. NH_4Cl per litre and padded on to cotton or viscose staple fibre gabardine at 30–35°c. The gabardine is dried and then baked for 5 min. at 140°c. This imparts a pleasant handle and good water repellent properties. C.O.C.

Dibenzoyl Alkyl Phenols for stabilising Polyester Resinous Compositions to Light

American Cyanamid *USP* 2,890,193

0·01–5·0% of a compound of formula—



(R^1 = Alk of 1–10 C; R^2 and R^3 = H, Alk of 1–4 C, alkoxy of 1–4 C or Hal), e.g. 2,6-dibenzoyl-4-methyl phenol, is used. C.O.C.

Antistatic Agents for Plasticised Resins

Dunlop Rubber Co. and Glovers (Chemicals) *BP* 820,541

Tertiary amines and their quaternary salts containing at least one oxyalkylene group and at least one long-chain aliphatic radical are excellent antistatic agents for use in plasticised synthetic resins. Thus artificial leather made from poly(vinyl chloride) containing dialphanyl phthalate (65 parts per 100 parts polymer) is given very good antistatic properties by adding 5% of $(C_{17}H_{33})N[(C_2H_4O)_5H]_2$ to the plastic composition. C.O.C.

Homologous Series of Surface-active Agents in Dry-cleaning (VII p. 624)
Printing Thickeners (IX p. 627)

IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

Complexes of Molybdate with Polyhydric Phenols

H. Buchwald and E. Richardson

Chem. and Ind., (25), 753 (20 June 1959)

Although some quant. data exist for the complexes of other ions with polyhydric phenols, none appears to be available for molybdenum and, following an investigation by Richardson (*J. inorg. nucl. Chem.*, **9**, 267 (1959)) on the reaction of molybdate and molybdic acid with certain polyhydroxy cpd., an extension has been made to embrace the polyhydric phenols. Whereas the former complexes are colourless, the intense colours given by the polyhydric phenols afford spectrophotometric data which indicate that in the pH range 4–7 a 2:1 phenol to molybdate complex is always found, whilst at lower pH values the composition of the complex varies according to the other subst. groups. H.H.H.

α-Naphthylamide of 3-Aminobenzenesulphonic Acid

A. Chrzaszczewska, Z. Milewska, and S. Pizon

Lodz. Towarz. Nauk, Wydział III, Acta Chim., **3**, 63–66 (1958) (in English): *Chem. Abs.*, **53**, 13117 (25 July 1959)

The reduction of *N*-(α-naphthyl)-3-nitrobenzenesulphonamide to the title product, useful as an azo dye intermediate, is effected by heating with alcoholic Na_2S. E.S.

N-(2-Hydroxyethyl)-N-(1-naphthyl)-3-Amino-6-Methylbenzenesulphonamide

M. Tarnowska *Lodz Towarz. Nauk, Wydział III, Acta Chim.*, **3**, 67–71 (1958) (in English): *Chem. Abs.*, **53**, 13117 (25 July 1958)

N-(β-hydroxyethyl)-1-naphthylamine condensed with 6-methyl-3-nitrobenzenesulphonyl chloride in ethanol in presence of sodium acetate gives the substituted amide. Fe-HCl reduction of the nitro group then gives the title product, an intermediate for azo dyes. E.S.

Direct Dyeing of Cellulose. VII—Relationship between the Dyeing Properties and the Conjugated System of Double bonds

K. Nishida *J. Soc. Textile Cellulose Ind. Japan*, **15**, 499–501 (June 1959)

The solubilities in water, coagulation values and absorption isotherms of Diamine Black RO (C.I. Direct Black 29) and Direct Violet O (C.I. Direct Violet 12) are given. The mean standard affinities of the black and the violet were 5·5 and 7·1 respectively. The violet has the greater affinity for cotton. These differences exist because: (1) use of J-acid yields dyes of higher affinity than those from γ-acid; (2) decrease in solubility increases the standard affinity or increases the precipitation of the dye. C.O.C.

Dyeing Properties of Acid Azo Dyes—III

M. Sekido and T. Iijima

J. Soc. Textile Cellulose Ind. Japan, **15**, 476–477 (June 1959)

An account of the dyeing properties of dyes having the same skeletal structure as dyes prepared from diazotised *p*-X-aniline coupled with J-acid [alkali coupling and acid coupling] (X = H, SO_3H, SO_2NH_2, COOH, $COOC_2H_5$, Cl, CH_3, OCH_3, NO_2, NH_2, and $NHCOCH_3$). The alkali-coupled dyes yield brighter dyeings on wool than the acid-coupled. All the dyes have good affinity for wool from a neutral bath. The exhaustions (SDC method) of these dyes are higher than those of dyes prepared from diazotised *p*-X-aniline and γ-acid. C.O.C.

Spectra of 1-(Phenylazo)-2-naphthol Derivatives containing Contrapolar Electron-donor Systems

V. A. Izmail'skiĭ and A. V. Malygina

Khim. Nauka i Prom., **4**, 279–280 (1959): *Chem. Abs.*, **53**, 15759 (10 Sept. 1959)

The absorption spectra of 1-(phenylazo)-2-naphthol (C.I. 12055) and its derivatives exhibit four bands. Substitution of CH_3 and CH_3O groups in the 2,5-positions of the benzene ring affected only the long-wave band,

λ_{max} = 475 mμ. The shift in λ_{max} caused by substitution was: 2,5-$(CH_3)_2$, +25 mμ.; 5-CH_3O, +30 mμ.; and 5-CH_3O and 2-CH_3, +35 mμ. Introduction of -$NHCOCH_3$ *n*-$NHCOC_6H_5$ (I) in position 4 did not affect λ_{max} of the 2,5-$(CH_3)_2$ derivative. I or -$NHCOC_6H_4NO_2$ in 4-positions of the 5-CH_3O-2-CH_3 derivative shifted λ_{max} + 45 mμ., whereas presence of I in 4- lowered λ_{max} of the 5-CH_3-2-CH_3O derivative. The results confirm that the contrapolar influence of 2 electron-donor groups para to each other increases the electron-donor capacity of the system and causes a bathochromic effect. C.O.C.

Spectra of 1-(Phenylazo)-3-(anilinocarbonyl)-2-naphthol containing Contrapolar Electron-donor Systems

V. A. Izmail'skiĭ and A. V. Malygina

Khim. Nauka i Prom., **4**, 280–1 (1959): *Chem. Abs.*, **53**, 15795 (10 Sept. 1959)

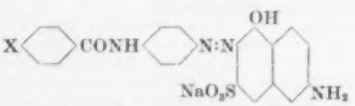
Presence of -$CONHC_6H_5$ in the naphthol ring decreased the bathochromatic shift shown by the 2-naphthol analogue (see previous abstract). The order of the reduced effects of the electron-donor groups was different, and the order differed in ethanol from that in pyridine. The different bathochromatic effects of the two analogues is ascribed to the probable quinone–hydrazone structure of the 3-hydroxy-2-naphthanilide (C.I. 37505) derivatives producing a strong electron-donor system and an opposing complex electrophilic quinonoid system in the same molecule. C.O.C.

Fastness to Light of some Monazo Dyes derived from Benzanilide and 2-Amino-5-naphthol-7-sulphonic Acid

V. A. Blinov, B. M. Krasovitskiĭ, and E. E. Khotinskaya

Khim. Nauka i Prom., **4**, 285–6 (1959): *Chem. Abs.*, **53**, 15570 (25 Aug. 1959)

Monazo dyes of formula



were prepared from benzanilide and its derivatives by coupling with 2-amino-5-naphthol-7-sulphonic acid in sodium carbonate solution. Fastness to light, using a 1–5 scale, was about the same, 3–4, for all the dyes when exposed to light alone. Tested for fastness to light and weather the dyes varied as follows (X and fastness given): H, 1; CH_3, 2; Br, 3–4; CH_3O, 3; $N(CH_3)_2$, 3; $COOC_2H_5$, 3; OH, 1. These data compare with a fastness to light of 1 for dyes prepared using aniline as the azo component and of 3–4 for dyes using 4-aminobiphenyl as azo component. C.O.C.

Substitution of Halogen Atoms in *o,o*-Dihalogeno-*o'*-hydroxy Azo Dyes

B. I. Stepanov and M. A. Andreeva

Nauch. Doklady Vysshei Shkoly, Khim. i Khim. Tekhnol., (1), 141–2 (1959): *Chem. Abs.*, **53**, 17066 (25 Sept. 1959)

Two Cl atoms in aromatic azo compounds situated in the same ring, in *o*-position to the azo group, in presence, in another ring, of a hydroxy group in *o*-position to the same azo group, and in presence of Cu salts, are readily substituted by alkoxy and aroxy groups, this substitution occurring much more readily than the substitution of one halogen atom in the analogous *o*-monohalogeno-*o'*-hydroxy azo compound. Thus, 2,6-dichloroaniline (10 g.) in conc. H_2SO_4 (32 ml.) is diazotised at 5°c. using $NaNO_2$ (4·5 g.) and conc. H_2SO_4 (32 ml.). The solution is diluted, cooled in ice, the diazo compound treated at 5–10°c. with 2-naphthol (9 g.), NaOH (52 g.), and water (200 ml.), the orange dye filtered off and dried to yield 93% 1-(2,6-dichlorophenylazo)-2-naphthol (I). To Na (0·34 g.) in butanol (10 ml.) is added a mixture of Cu acetate (0·25 g.) in butanol (40 ml.) and I (0·8 g.) in toluene (50 ml.) and the whole refluxed while stirring for 30 min. at 100°c., 10% H_2SO_4 (60 ml.) is added, the solution dried over Na_2SO_4, the solvent evaporated *in vacuo* and the precipitate filtered off, washed with methanol and dried to yield 98% of the red dibutoxy anologue of I. To Na (0·046 g.) and 4-hydroxybiphenyl (0·51 g.) in dioxane (10 ml.) at 100°c. is added a mixture of I (0·16 g.) in dioxane (7 ml.) and Cu acetate (0·05 g.) in dioxane (8 ml.). The whole is refluxed at 100°c. for 4 hr., 10% H_2SO_4 (20 ml.) is added, the red precipitate filtered off, washed with water, treated with 1% NaOH while heating to remove excess 4-hydroxybiphenyl, the residue filtered off, washed with water till neutral to Brilliant Yellow and dried to yield 0·29 g. of the orange-red 1-[2,6,di(*p*-biphenyloxy)phenylazo]-2-naphthol. C.O.C.

Kinetics and Mechanism of Diazotisation. XIV—General Equation for the Velocity of Diazotisation of Aniline in Perchloric Acid, and a Discussion of the Mechanism of Diazotisation

H. Schmid and C. Essler

Mh. Chem., **90**, 222–231 (21 April 1959)

The general velocity equation for the diazotisation of aniline in perchloric acid soln. (concn. 0·05–4 mol./l.) is given as

$$\frac{d(C_6H_5N_2^+)}{dt} = [C_6H_5NH_3^+][HNO_2]\left(k_1 + k_2\frac{[HNO_2]}{[H^+]} + \frac{m\cdot\gamma^2}{a_{H_2O}}(k_3 + k_4 m)\right)$$

where m = molality, γ = activity coeff. of perchloric acid, and a_{H_2O} = activity of the water in the acid soln. At 0°c. the constants are per min.: $k_1 = 2$; $k_2 = 450$; $k_3 = 2$; $k_4 = 1{\cdot}75$. Under 0·05 mol./l. the term $k_2\frac{[HNO_2]}{[H^+]}$ becomes $\frac{k'[HNO_2]}{k''[H^+] + [C_6H_5NH_3^+]}$ with $k' = 45$ and $k'' = 0{\cdot}1$ per min. at 0°c. The acids in which diazotisation can be carried out fall into two groups, viz. those in which the velocity term with k_4 plays an insignificant part, so that at a definite acid concn. there is a max. velocity of diazotisation, and those for which k_4 is important and where no such optimum acid concn. exists. After discussion of the separate velocity terms, the reaction scheme previously proposed by Schmid and Woppmann (*Mh. Chem.*, **88**, 411 (1957)) has been revised accordingly, and now reads as follows—

(*a*) $RNH_3^+ + H_2O \longleftrightarrow RNH_2 + H_3O^+$

(*b*) $HNO_2 + H_2O \longleftrightarrow NO_2^- + H_3O^+$

(*c*) $HNO_2 + H_3O^+ \rightleftharpoons H_2ONO^+ + H_2O$

(*d*) $H_2O{\cdot}NO^+ + NO_2^- \rightleftharpoons N_2O_3 + H_2O$

(*e*) $H_2O{\cdot}NO^+ + ClO_4^- \rightleftharpoons NOClO_4$ ($NOCl$, $NOBr$, N_2O_4) + H_2O (or Cl^-, Br^-, NO_3^-)

(*f*) $H_2O{\cdot}NO^+ + RNH_2 \rightarrow RNH_2NO^+ + H_2O$

(*g*) $N_2O_3 + RNH_2 \rightarrow RNH_2NO^+ + NO_2^-$

(*h*) $NOClO_4 + RNH_2 \rightarrow RNH_2NO^+ + ClO_4^-$, ($Cl^-$, Br^-) (or NOCl, NOBr)

(*i*) $NOClO_4$ (or N_2O_4) + $RNH_3^+ \rightarrow RNH_2NO^+ + H^+ + ClO_4^-$ (NO_3^-)

(*j*) $H^+ + H_2O \longleftrightarrow H_3O^+$

(*k*) $RNH_2NO^+ + H_2O \rightarrow RNHNO + H_3O^+$

(*l*) $RNHNO \rightarrow RN_2OH$

(*m*) $RN_2OH \rightarrow RN_2^+ + OH^-$

(*n*) $OH^- + H_3O^+ \longleftrightarrow 2H_2O$

H.H.H.

Mechanism of Replacement of the Aromatic Diazonium Group by Iodine

J. G. Carey, G. Jones, and I. T. Millar

Chem. and Ind., (32), 1018–1019 (8 Aug. 1959)

It has been previously suggested (cf. Hodgson, Birtwell, and Walker, *J.C.S.*, 770 (1941)) that a diazonium ion on addition to a solution of an iodide acts as an oxidant giving rise to iodine and thus to the tri-iodide ion, which then reacts with more diazonium ion to give aryl iodide and nitrogen with regeneration of iodine. When tri-iodide formation is prevented, the diazonium ion does not react with the mono-iodide. Two examples are now recorded in which intermediate diazonium tri-iodides have been isolated, viz. *o*-toluene- and mesitylene-diazonium tri-iodide dihydrate, and thus relate the ready formation of aryl iodides from diazonium soln. and iodides, in contrast with the general need for a cuprous or other catalyst with other halides, to the ease of oxidation of iodide to the halogen, and to the formation therefrom of a highly polarisable complex anion, able to effect replacement of nitrogen in the diazonium ion. H.H.H.

Light Absorption of Five and Five-six Membered Orthocondensed Heterocyclic Compounds

A. I. Kiss and B. R. Muth

Magyar Tudományos Akad. Központi Fiz. Kutató Intézetének Közleményei, **3**, 441–7 (1955): *Chem. Abs.*, **53**, 15760 (10 Sept. 1959)

The mechanisms of light absorption by 5- and 5–6-membered orthocondensed rings are entirely different, corresponding to the different properties of these compounds. The spectrum of the basic hydrocarbon not containing a hetero atom is different from that containing a hetero atom, and is similar to the corresponding aliphatic hydrocarbon. Presence of the hetero atom in the molecule results in a new, uniform electron configuration; this gives the compound aromatic characteristics that yield a different spectral structure. The bathochromic shift in the spectrum is proportional to the negativity of the hetero atom. C.O.C.

Triphenylmethane Dyes from Guaiacol

J. Gronowska *Wiadomości Chem.*, **13**, 153–166 (1959): *Chem. Abs.*, **53**, 16542 (10 Sept. 1959)

Review, 44 references. C.O.C.

Orange Sulphur Dyes

P. Yien *Hua Hsüeh Shih Chieh*, **2**, 74–5 (1959): *Chem. Abs.*, **53**, 15571 (25 Aug. 1959)

o-Dianisidine (1 mol.) is diazotised at 0–2°c. and coupled with 1-naphthylamine (2 mol.) at 10°c. The product (1 mol.) is treated with cyanuric chloride at 0–3°c. for 1 hr. keeping the solution weakly alkaline to litmus by addition of 10% aq. Na_2CO_3. This intermediate product (1 mol.) is treated with thiourea (4 mol.) at 40–45°c. for 3–4 hr., or at 45–90°c. for 1–2 hr. or 90–95°c. for 3–4 hr., keeping neutral to litmus by additions of 10% aq. Na_2CO_3, to yield an orange sulphur dye having affinity for nylon and cotton. C.O.C.

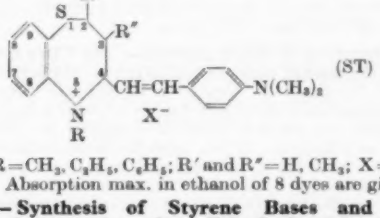
Cyanine Dyes from Seven-membered Heterocyclic Rings

L. K. Mushkalo

I—Styrenes in the Series of Dihydrobenzohepta-1,5-thiazine

Zhur. obshch. khim., **29**, 1030–34 (March 1959)

Quaternary salts of the derivatives of dihydrobenzohepta-1,5-thiazine, containing a methyl group in the 4-position, readily condense with *p*-dimethyl aminobenzaldehyde and *p*-hydroxybenzaldehyde with the formation of the corresponding styrenes (ST)—



(ST)

where R = CH_3, C_2H_5, C_6H_5; R′ and R″ = H, CH_3; X = ClO_4, Br, I. Absorption max. in ethanol of 8 dyes are given.

II—Synthesis of Styrene Bases and their Analogues in the Dihydrobenzohepta-1,5-thiazine Series

Ibid., 1034–1042

It has been found that ST is more deeply coloured than the corresponding base, an identical effect occurring with hydroxy benzenes and also with furan and pyrrole analogues of ST. The introduction of nitro and acetylamino groups in the 8-position slightly deepens the colour. Substitution of R by H does not affect the colour. G.J.K.

Pyridine Dyes—Derivatives of Secondary Amines

N. E. Grigor'eva, I. K. Gintse, and Z. M. Afanas'eva

Zhur. obshch. khim., **29**, 865–869 (March 1959)

Four *N*-substituted pyridine dyes and two monoanils of glutaconic aldehyde have been prepared. The absorption spectra (200–550 mμ.) of three *N*-substituted dyes have been investigated and a suggestion is made that colour depth and hydrolysis effects (excess alkali) are due to steric hindrances, which in turn indicate a cyclic structure for these dyestuffs. G.J.K.

Asymmetric Pyridine Dyes

N. E. Grigor'eva, V. N. Voinova, and L. M. Dukina

Zhur. obshch. khim., **29**, 935–940 (March 1959)

16 new asymmetric pyridine dyes (I) have been synthesised using standard technique (T. Zincke, *Lieb. Ann.*, **338**, 107 (1905)). From a comparison of the absorption max. (ultraviolet) of I with the corresponding symmetrical dyes (II) a relation between colour and basicity of the amine in the dye molecule has been observed for most cases. The absorption max. of I and II, together with yields and analytical data, are tabulated. G.J.K.

Synthesis of Thiacarbocyanines from 5-substituted 2-Methyl-6,7-tetramethylbenzthiazole

M. A. Al'perovich, Z. I. Miroshnichenko, and I. K. Ushenko

Zhur. obshch. khim., **29**, 989–997 (March 1959)

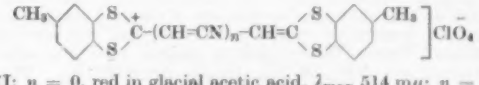
Eleven derivatives of 2-methyl-6,7-tetramethylene benzthiazole have been synthesised and some quaternary salts and thiacarbocyanines prepared from them. It is shown that the introduction of ethoxy and methoxy groups in 5,5′-positions of 6,7,6′,7′-bis-tetramethylene carbocyanine causes a bathochromic displacement of the absorption max. by 24 mμ. G.J.K.

Benzodithiylium Dyes—I

L. Soder and R. Wizinger

Helv. chim. Acta., **42**, 1733–1737 (3 Aug. 1959)

Starting from toluene dithiol, the preparations of several simple 1,3-benzdithiylium (1,3-dithiahydrindenium) salts are described and used for the subsequent synthesis of bis-5-methyl-1,3-benzdithiylium-mono- and -trimethincyanine-perchlorate (I). The replacement of $-NC_5H_5$ in the classical cyanines by –S– has a strong bathochromic effect of about 90–110 mμ. throughout the series.



(I: $n = 0$, red in glacial acetic acid, λ_{max} 514 mμ; $n = 1$, greenish-blue in glacial acetic acid, λ_{max} 666 mμ).

H.H.H.

Structure of the Primary Condensation Product in the König Dye Synthesis

S. Creyf and L. Roosens

Symposium over kleur en Struct. Org. Verbindungen, *Antwerp*, 56–68 (1956): *Chem. Abs.*, **53**, 6070 (10 April 1959)

Reaction of BrCN with nicotinamide in presence of moisture does not yield the *N*-cyano-3-carbamido-2-pyridine as reported by Douzou and LeClerc (*Chem. Abs.*, **49**, 10128 (1955)) but opens the pyridine ring in the 1–2 position to yield $NCNHCH{:}CHCH{:}C(CHO)CONH_2$ (I). Ultraviolet spectra in water at pH 9 show I cannot have an α- or γ-pyridone structure but has an unsaturated chain similar to that in furfurylpentanedienal. C.O.C.

Fluorescent Brightening Agents of the Triazylstilbene Series

A. Yabe and M. Hayashi

II—Combined Derivatives of Amino and Hydroxyl Groups

Kōgyō Kagaku Zasshi, **60** 1546–1562 (1957): *Chem. Abs.*, **53**, 15571 (25 Aug. 1959)

The intensity of fluorescence of 0·0001–10·0% solutions effects of temperature (20–90°c.), time of application (5–60 min.) and amount of NaCl used (0–20% on the fibre) were examined for this effect on the brightening action of compounds of formula Na 4,4′-bis (2-X-4Y-1,3,5-triazinylamino)-2,2′-stilbenedisulphonic (X and Y = OH and NH_2 (I), OH and NHC_6H_5; OH and $NC_6H_4SO_3Na$ (II), OCH_3 and NH_2; OCH_3 and NHC_6H_5; OCH_3 and $NHC_6H_4SO_3Na$; OC_2H_5 and NH_2; OC_2H_5 and NHC_6H_5; OC_2H_5 and $NHC_6H_4SO_3Na$). Fluorescence is usually at a maximum in 0·1% solution. Temperature and time have different effects in the individual agents but addition of NaCl generally improves the brightening effect. The fastness to light of the agents is good except for I and the fastness to washing is satisfactory except for II. The most promising agents considered from general characteristics are when X and Y are OH and NHC_6H_5, OCH_3 and NHC_6H_5, OCH_3 and $NHC_6H_4SO_3Na$, OC_2H_5 and NH_2, OC_2H_5 and NHC_6H_5.

III—Combined Derivatives of Different Amino or Hydroxyl Groups

Ibid., **61**, 78–82 (1958):
Chem. Abs., **53**, 16542 (10 Sept. 1959)

Compounds of formula di-Na 4,4′-bis(2-X-4-Y-1,3,5-triazin-6-ylamino)-2,2′-stilbenedisulphonate were examined for fluorescence intensity in 0·001–1·0% concentration with or without Na dodecyl sulphate, carboxymethyl cellulose or NaCl. The temperature coefficient (20–90°c.) of fluorescent intensity, variation of fluorescent intensity with time of application, fastness to light and to washing were determined for the compound where X and Y = NH_2, NHC_6H_5; NHC_6H_5, $NHC_6H_4SO_3Na$; $NHC_6H_4SO_3Na$, NH_2; OH, OCH_3; OCH_3, OC_2H_5; and OC_2H_5, OH. The first three amino derivatives have nearly the same fluorescent intensity as similar derivatives containing the same two amino groups X and X. The fastness to washing was generally better than that of the X,X amino derivatives. Fastness to light was poor. Derivatives with different OH, OCH_3 or OC_2H_5-groups were recognisably inferior in fluorescence to the (X,X) hydroxyl-derivatives but had somewhat better fastness to light and washing. With the exception of the NHC_6H_5, $NHC_6H_4SO_3Na$ derivatives which has reasonably high fluorescence and fastness the compounds examined seem to have no practical value.

IV—Effects of Substituents on Fluoresence and Substantivity of Triazinylstilbene Fluorescent Brightening Agents

Ibid., 82–9:
Chem. Abs., **53**, 16542–3 (10 Sept. 1959)

Results of tests made with 21 compounds of the above formula (X and Y = any combination of two of the following: NH_2, NHC_6H_5, $NHC_6H_4SO_3Na$, OH, OCH_3 and OC_2H_5) are summarised. All had maximum absorption bands at 340–365 mμ.; the position of the 2nd absorption band is sometimes characteristic of the substituted radicals. Strong fluorescence is shown when the substituents are NH_2, OCH_3, OC_2H_5 or NHC_6H_5. The (X,Y) combinations between each of OH, OCH_3 and OC_2H_5 with NH_2, NHC_6H_5 and $NHC_6H_4SO_3Na$ gave compounds with strongest fluorescent intensity. Addition of NaCl usually considerably increased the fluorescence whereas Na dodecyl sulphate or carboxymethylcellulose had no noticeable effect. Applications at higher temperatures and for a longer time increased the exhaustion except for compounds containing hydrophilic radicals. Some decomposition of the compounds was noticed in very dilute baths. Fastness to light was noticeably improved by OCH_3 and OC_2H_5 radicals. The best group of products were those where (X,Y) = (OCH_3, NHC_6H_5), (OC_2H_5, $NHC_6H_4SO_3Na$) and (OC_2H_5, NH_2), the next best group being (OC_2H_5, NHC_6H_5), (NHC_6H_5, $NHC_6H_4SO_3Na$), (OC_2H_5, OC_2H_5) and (OCH_3, $NHC_6H_4SO_3Na$) C.O.C.

Thioindigo Dyes. II—Bromination of *S*-aryl Thioglycollic Acids

G. M. Oksengendler and Yu. E. Gerasimenko
Zhur. obshch. khim., **29**, 919–924 (March 1959)

Bromination of *S*-aryl thioglycollic acid (I) under irradiation (ultraviolet) yielded new *α*-bromo-*S*-aryl thioglycollic acids which hydrolyse to bis-(aryl thio)-acetic acids.

In the absence of irradiation and with catalysts (e.g. I_2), nuclear bromination of I occurs yielding a series of products which are tabulated. G.J.K.

Metal Phthalocyanines in Solution. I—Stability of the Phthalocyanines of a Few Metals of the Middle of the Fourth Period

B. D. Berezin *Izvest. Vysshikh Ucheb. Zavedenii, Khim. i Khim. Tekhnol.*, **2**, (1), 10–14 (1959):
Chem. Abs., **53**, 16663 (25 Sept. 1959)

The thermodynamic stability of phthalocyanine (I) metal (M) complexes in solution is characterised by the equilibrium constant (K) in the equation—

$$(MI)_{sol} + 2H_3O^+ \rightleftharpoons (H_2I)^{2+}{}_{sol} + 2H_2O$$

With Cu and Co phthalocyanines at 20–70°c. K is of the order of 10^{-6}. Data for the above reaction prove that Ni^{2+} and not Co^{2+} has the maximum stability in MI for the middle of the period. The low solubility of MI (M=Cu^{2+}, Ni^{2+} and Co^{2+}) according to the reaction indicates a very slight exchange between M^{2+} and H ions and this suggests that in preparing Cu^{2+}, Ni^{2+}, and Co^{2+} phthalocyanine pigments, treatment with H_2SO_4 up to 7–8 moles/l. has no relationship with the losses of phthalocyanine by solution or to the loss of colour caused by accumulation of molecules of metal-free phthalocyanine or to its decomposition. Studies of solubility show extraordinary stability of the phthalocyanine complexes of the metals of the middle of the fourth period from Co^{2+} to Zn^{2+}. Apparently these metals form stable covalent dsp^2-hybrid bonds with phthalocyanine; this is confirmed by the corresponding magnetic data for Co and Ni phthalocyanines. C.O.C.

Copper Phthalocyanine (C.I. 74160) Polymers.

W. C. Drinkard and J. C. Bailar
J. Amer. Chem. Soc., **81**, 4795–4797 (20 Sept. 1959)

Polymeric copper phthalocyanines have been produced by reacting pyromellitic dianhydride, $CuCl_2$, urea and catalyst at 180°c. Products of average mol.wt. as high as 4000 have been identified. The polymers are linear without exception but so far it has not been possible to determine whether they are straight or "zig-zag" chains. Because of the large weight of a single unit, a polymer of mol.wt. 4000 has a chain of only 6 units. C.O.C.

Manganese Phthalocyanine as an Oxygen Carrier

J. A. Elvidge and A. B. P. Lever
Proc. Chem. Soc., 195 (June/July 1959)

Manganese phthalocyanine (I) can combine reversibly with oxygen and appears to be the first example of a Mn cpd. that behaves as an oxygen carrier. The reaction now examined is that of a soln. of I in pyridine (necessarily $\leq 5\times10^{-4}$ molar) which absorbs oxygen in the cold, turning from olive-green (λ_{max} 7125A.) to dark blue (λ_{max} 6200A.); on boiling, the green soln. reappears to reabsorb oxygen on cooling. The cycle can be repeated many times with little destruction of the pigment. It is found that pyridine plays an essential part and cannot be replaced by non-donor solvents such as *o*-dichlorobenzene. The oxygen uptake is 1 mol. per 2 mol. I, and the isolated product has the formula $C_{32}H_{16}N_8MnO{\cdot}py$ (py = pyridine) and possesses a quadrivalent structure. A reaction scheme is suggested. The mode of combination with oxygen is different from that for haemoglobin. I readily decomposes H_2O_2 but is itself fairly rapidly destroyed; it catalyses efficiently the aerial oxidation of benzaldehyde and aniline. H.H.H.

List of Food Dyes acceptable in Twenty-one Countries

C. Nieman
Zucker- u. Süsswarenwirtsch., **12**, 300–304 (1959):
Chem. Abs., **53**, 17349 (25 Sept. 1959)

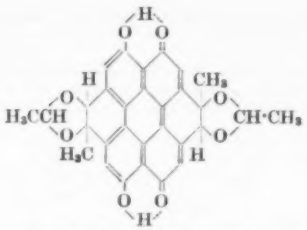
Tables giving the dyes accepted for use for colouring food in 21 different countries. C.O.C.

The Pigments of Black Aphids—The Chromophore of Erythroaphin and Constitution of Hypericin

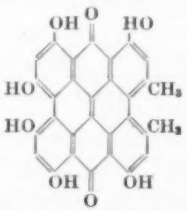
R. I. T. Cromartie *Research*, **12**, 335–339 (Sept. 1959)

Living aphids contain protoaphin which is deep crimson in neutral or alkaline solution changing reversibly to yellow at pH<5·5. It can only be isolated from aphids that have been killed by treatment with water at 70°c. to destroy an enzyme present in the insect which converts the protoaphin in presence of air successively into three ether soluble fluorescent pigments which are in order of appearance, yellow, orange, and red respectively. These pigments seem all to be various types of erythroaphins in which the chromophore is 4,9-dihydroxyperylene-3,10-quinone—

Four possible formulae are given for eryothroaphin of which it is considered—



is the more likely. Its polycyclicacromatic system is surpassed in complexity among natural products only by hypericin—



the quinonoid pigment present in *Hypericum* spp. (St. John's wort) the constitution of which has been established by H. Birckmann and his collaborators (*Fortschr. Chem. org. Naturst.*, **14**, 191 (1957)). The two pigments have many chemical and physical properties in common, erythroaphin even showing some of the characteristic photodynamic activity of hypericin. 15 references.

C.O.C.

Isolation of Berberine (C.I. 75160) from the Roots of *Berberis vulgaris* and its Chromatographic Testing

E. Pawlczyk, J. Pawlczyk, A. Smrakiewiczowa, and F. Adamanis *Chem. Anal.* (Warsaw), **4**, 265–268 (1959): *Chem. Abs.*, **53**, 17427 (25 Sept. 1959)

Isolation of Berberine from plant roots is described and the results of its chromotographic analyses compared with those obtained with Merck Berberine and with those obtained by Chattajee (*Chem. Zentr.*, **123**, 5113 (1952)). There was good agreement. C.O.C.

Preparation and Degradation Products of Betanidin

H. Wyler and A. S. Dreiding *Helv. chim. Acta*, **42**, 1699–1702 (3 Aug. 1959)

The earlier described betanidin (cf. Ainley and Robinson, *J.C.S.*, 446 (1937)) has been resolved by paper chromatography from buffer soln. of potassium and ammonium acetate–acetic acid respectively into (probable) isomeric dye components now designated betanidin and *iso*-betanidin, for which the empirical formulas ($C_{19}H_{18-20}O_8N_2$) are deduced. Degradation by zinc dust distillation and by alkali fusion has afforded indole and pyridine cpd., but it is not yet established whether the indole or pyridine ring system is present in betanidin. H.H.H.

Constitution of Betanin

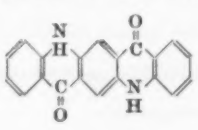
H. Wyler, G. Vincenti, M. Mercier, G. Sassu, and A. S. Dreiding *Helv. chim. Acta*, **42**, 1696–1698 (3 Aug. 1959)

Crystalline specimens, which exhibit the same absorption spectrum in water, have been prepared of the beet dye betanin from buffer soln. of potassium acetate–acetic acid, ammonium acetate–acetic acid, and pyridine–formic acid respectively. From them, the empirical formula, $C_{23}H_{28-30}O_{13}N_2$, has been derived, and certain structural features are also reported, such as the presence of a basic and a strong acid group to produce a zwitterion. In the beet, betanin is accompanied by three related violet cpd. H.H.H.

Light-fast Quinacridone Red Pigments

T. B. Reeve and E. C. Botti *Off. Dig. Fed. Paint Varn. Prod. Cl.*, **31**, 991–1002 (July 1959)

The Monastral (DuP) reds and violet are based upon quinacridone—



Their outstanding brightness and fastness to a wide range of agencies, coupled with their compatibility with other pigments, ranks them with the phthalocyanines. There are diagrams showing their relative transparency in masstone, and their reflectance curves both in masstone and in reduction. Three tables show their properties in several media and compare them with those of several other pigments in the same media; two others indicate their economic and performance advantages in industrial baking enamels. Their properties are discussed under the following headings: durability, chemical resistance, resistance to bleeding in organic solvents, heat resistance, colour stability in storage, rheological behaviour, dispersibility, and blending and toning applications.

J.W.D.

Effect of Cations and Anions of Substances Determining the Properties of Yellow Ferric Oxide (C.I. 77492)

M. Kranz and A. Witkowska *Przemysl Chem.*, **38**, 88–91 (1959): *Chem. Abs.*, **53**, 16653 (25 Sept. 1959)

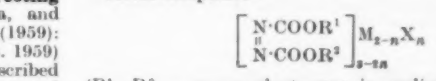
Study of the effect of anions connected with Cd^{2+} (highly active as trace substances that determine the hue and properties of Fe_2O_3) and of K^+ and Na^+ (inactive) permits elimination of the action of cations so that the behaviour of SO_4^{2-}, NO_3^-, CH_3COO^-, Cl^-, Br^-, and I^- can be examined. The anions of the trace substances as well as the cations exert a selective effect on the properties of yellow Fe_2O_3. The effect is caused by the joint action of the cation and the anion. Generally the action of anions alone is less energetic and sometimes less advantageous than that of anions connected with Cd^{2+}. C.O.C.

PATENTS

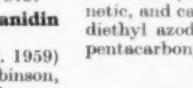
Metal-complexes of Azo Diformate Esters

DuP *USP* 2,882,268

Metal complexes—



(R^1, R^2 = monovalent organic radicals of up to ca. 12 C; X = a monovalent carbonyl substituting group, e.g. H, Hal, cyanyl, and nitrosyl; M = a group VIII metal; $n = 0$ or 1) on pyrolysis give pyrophoric, generally magnetic, and catalytically active finely-divided metals. Thus diethyl azodiformate in cyclohexane is stirred with iron pentacarbonyl to give a blue-black precipitate of

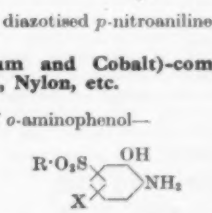


E.S.

Monoazo Disperse Dyes

Pittsburgh Coke & Chemical Co. *USP* 2,882,269

Styrene oxide (I) or its homologues are condensed with primary and secondary aromatic amines to give products which couple with suitable diazo compounds to give disperse dyes. Thus *N*-methylaniline is refluxed in xylene with I and a little acetic acid to give

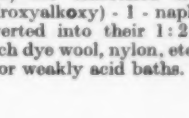


Coupling with diazotised *p*-nitroaniline then gives a red disperse dye. E.S.

Metal(Chromium and Cobalt)-complex Monoazo Dyes for Wool, Nylon, etc.

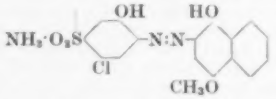
S *BP* 820,158

Derivatives of *o*-aminophenol—



(X=H, Hal or Alk of 1–4 C; R=Alk of 1–4 C, or subst. or unsubst. amino) are diazotised and coupled with 4-alkoxy(or hydroxyalkoxy)-1-naphthols, and the products are converted into their 1:2 metal-complexes with Cr or Co, which dye wool, nylon, etc. blue, green, and grey from neutral or weakly acid baths. Thus diazotised

2-amino-4-chlorophenol-5-sulphonamide is coupled with 4-methoxy-1-naphthol in aq. NaOH to give—



Heating with aq. $CoSO_4$ in presence of NaOH and tartaric acid gives the Co-complex which dyes wool and nylon blue. E.S.

Metal(Chromium)-complexes of Mixtures of Monoazo Dyes, for Wool, Nylon, etc.

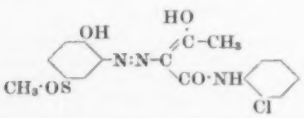
Ciba *BP* 820,489

Complexes containing 1 atom of Cr to 1 mol. of a monoazo compound anthranilic acid→β-naphthol (substituents other than COOH and SO_3H may be present) and 1 mol. of an *oo'*-dihydroxymonoazo or *o*-carboxy-*o'*-hydroxymonoazo compound free of SO_3H and of COOH other than in *o*-position to the azo group, dye wool, nylon, etc. from neutral or weakly acid baths. Thus 1 mol. each of the monoazo compounds anthranilic acid→β-naphthol and anthranilic acid→3-methyl-1-phenyl-5-pyrazolone are boiled in aq. *n*-butanol with sodium chromosalicylate. The product dyes wool brown. E.S.

Metallisable and Metal-complex Monoazo Dyes for Wool, having Alkylsulphoxide Groups

Gy *BP* 820,502

Presence of an alkyl- or cycloalkyl-sulphoxide group SO·Alk) in a 1:2 metal-complex monoazo dye structure free of SO_3H groups confers a higher degree of hydrophilic character than does the widely-used alkylsulphonyl group (SO_2·Alk), thus giving dyes of improved solubility and level-dyeing properties. Thus 2-aminophenol-4-methylsulphoxide is diazotised and coupled with acetoacet-*o*-chloroanilide to give

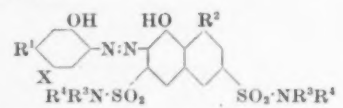


which dyes wool yellow by the single-bath chroming method. Heating with cobalt sulphate in presence of aq. tartaric acid gives the Co-complex, which dyes wool and nylon yellow from a weakly acid bath. Methods of preparation of suitable diazo and coupling components containing an SO·Alk group are outlined. E.S.

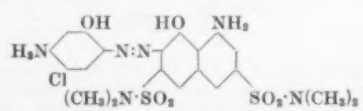
Green-blue Metallisable Monoazo Dyes for Wool and Nylon

General Aniline *BP* 816,991

Monoazo dyes—



(R^1, R^2 = NH_2, acylamino, Alk·SO_2·NH, or Ar·SO_2·NH, but R^2 is not NH_2 when R^1 = acylamino; R^3, R^4 = H, alk, or hydroxyalkyl of 1–4 C, or together form part of a heterocycle; X = H, Cl, or Br) may be metallised in substance or on wool and nylon to give green-blues. Thus 2-amino-4-chloro-5-nitrophenol is diazotised and coupled with 1-acetamido-3,6-di(*NN*-dimethylsulphamyl)-8-naphthol, and the monoazo compound so formed is chromed by heating in formamide with chromium formate. The nitro group is then reduced by heating with aq. Na_2S, to give the Cr-complex of

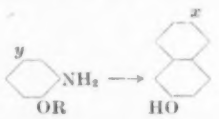


which is made into a dispersion by kneading with a formaldehyde/naphthalene-β-sulphonic acid condensate. E.S.

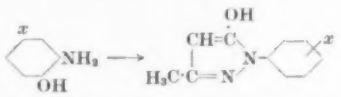
Brown Metal(Chromium)-complex Monoazo Dyes for Wool and Nylon

DuP *USP* 2,885,392

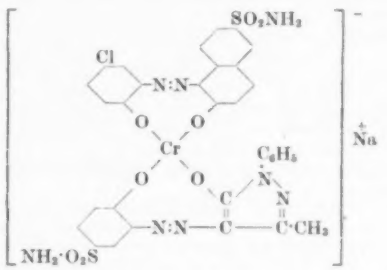
Mixed metal-complexes are made by heating together in a water soluble alcohol e.g. ethylene glycol, one mol. of a 1:1 chromium complex of a monoazo compound—



(*x* = H, SO_2·NH_2, or SO_2Alk; *y* = H or Cl; R = Alk of 1–6 C) and 1 mol. of an unmetallised pyrazolone azo compound



Alternatively the pyrazolone azo compound in the form of its 1:1 chromium complex is heated with an appropriate metal-free benzene-azo-naphthalene compound. The products contain 1 atom of Cr to 2 mol. of azo compounds, and dye wool and nylon brown from neutral or weakly acid baths. Thus the monoazo compound 2-amino-4-chloroanisole→2-naphthol-6-sulphonamide is heated in ethylene glycol at 140°C. with $CrCl_3$ to give the 1:1 Cr-complex. The mixture is cooled to 80°C. and 1 mol. of the monoazo pyrazolone compound 2-aminophenol-4-sulphonamide→3-methyl-1-phenyl-5-pyrazolone is then added and heating continued at 140°C., adjusting the pH value to 7·5 by addition of aq. NaOH, to give the mixed complex—

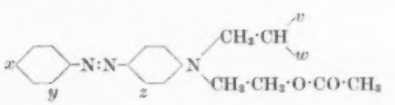


E.S.

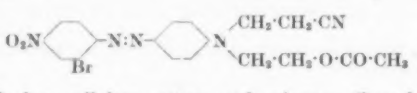
Monoazo Disperse Dyes

S *BP* 819,664

Monoazo disperse dyes—



(*x* = NO_2 or SO_2·CH_3; *y* = H, Cl, Br, CN, CF_3, SO_2·CH_3, or SO_2F; *z* = H or CH_3; *v* = H or F; *w* = F or CN), prepared by acetylating the corresponding *N*-β-hydroxyethyl-monoazo compounds, give oranges and reds on cellulose acetate, polyamide, polyester, and polyacrylonitrile fibres and reds and violets are given by similar dyes in which the diazo component is a naphthalene or S-containing heterocyclic amine, e.g. 2-aminothiazole. Thus the monoazo compound 2-bromo-4-nitroaniline→*N*-β-cyanoethyl-*N*-β-hydroxyethylaniline is boiled with acetic anhydride to give—

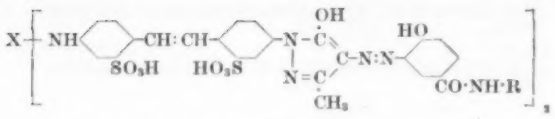


which dyes cellulose acetate and polyester fibres bright scarlet. E.S.

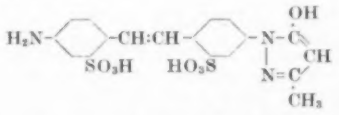
Yellow, Metallisable Disazo Stilbene Direct Dyes

Ciba *BP* 820,950

Stilbene diazo compounds—



(X = OC·CH:CH·CO or CO; R = benzene series radical free of SO_3H or COOH) may be metallised with Cu or Ni compounds, in substance or on cellulose. Thus 2 mol. of the stilbene pyrazolone—

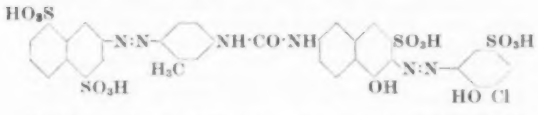


are condensed with 1 mol. of phosgene, and the urea derivative so formed is coupled with 2 mol. of diazotised 2-aminophenol-4-carbonanilide to give the disazo dye (X = CO; R = C_6H_5), which dyes cotton reddish yellow by the single- or two-bath aftercoppering process. E.S.

Metal(Copper)-complex Diazo Direct Dyes

FBy *BP* 819,841

Asymetric ureas $R^1{\cdot}N{:}N{\cdot}R^2{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}R^3{\cdot}OH$ (R^1, R^2 = naphthalene series radical; R^3 = aryl in which the azo link is in *p*-position to the urea group) are coupled, *ortho* to the OH group in R^3, with diazo compounds having *ortho* to the diazo group a group capable of metal-complex formation (e.g. OH, COOH, OAlk) to give disazo compounds whose copper complexes dye cellulose brown, red, and violet. Thus the urea formed by condensing the phenylurethane of the monoazo compound 2-naphthylamine-4,8-disulphonic acid→*m*-toluidine with J-acid is coupled in alkaline aq. pyridine with diazotised 2-amino-6-chlorophenol-4-sulphonic acid giving—

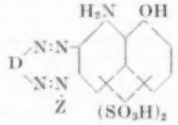


Heating with aq. $CuSO_4$ gives the metal-complex which dyes cellulose reddish brown. E.S.

Black Trisazo Dyes for Leather

CFM *BP* 820,199

A diazomonoazo compound—

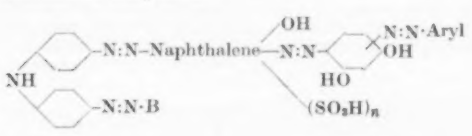


(D = residue of an aromatic diamine; Z = an acid radical) is combined in a neutral or alkaline medium with a diazo-arylsulphonamide, to form a diazodisazo compound which is then coupled with 1 mol. of a *m*-aminophenol. The products dye leather reddish black and give better penetration than similar dyes without a sulphonamide group. Thus a soln. of 1 mol. of diazotised metanilamide is added to 1 mol. of the diazomonoazo compound from 1 mol. of tetrazotised benzidine and 1 mol. of H-acid. Aq. Na_2CO_3 is then added, followed by an aq. soln. of 1 mol. of *m*-aminophenol, the trisazo dye being isolated by heating, neutralising, and salting out. E.S.

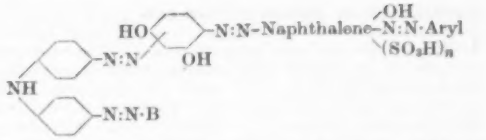
Brown Tetrakisazo Dyes for Leather

CFM *BP* 819,840

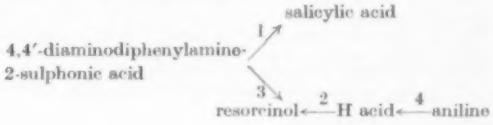
Tetrakisazo compounds—



or



(the diphenylamine residue contains at least one SO_3H; B = residue of a coupling component; *n* = 1 or 2; the benzene nucleus of the resorcinol residue may be dihydrogenised), and their Cu-complexes, may be made by a variety of methods, and dye leather deep, well-penetrated browns. An example is—

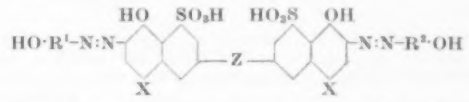


E.S.

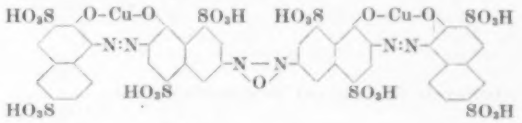
Metal(Copper)-complex Polyazo Direct Dyes

FBy *BP* 820,472

Copper-complexes of compounds—



(X = H or SO_3H, Z = azo or azoxy link; R^1, R^2 = residue of coupling components which couple *ortho* to the OH groups) dye cellulose grey, blue, green, and brown. They are made e.g. by diazotising a suitable nitro-naphthylaminesulphonic acid with an *ortho*-coupling phenolic or enolic coupling component, coppering the monoazo compound so formed under oxidising conditions, and then reducing, e.g. with NaOH and glucose, to form an azo or azoxy bridge between 2 mol. of the monoazo compound. Thus 6-nitro-2-naphthylamine-4,8-disulphonic acid is diazotised and coupled with R-acid, and the monoazo compound is stirred at pH 5·5 with $CuSO_4$ and hydrogen peroxide at 55–60°c. Reduction with aq. NaOH and glucose then gives—

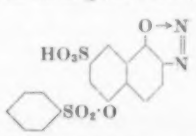


which dyes cotton blue. E.S.

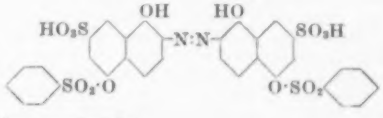
Diazo-oxides of the Naphthalene Series

FBy *BP* 819,667

Oxidation with e.g. chlorine water of naphthalene diazonium salts having SO_3H *ortho* to the diazo group and either (*a*) an arylazo group in the 4-position or (*b*) an arylsulphonyloxy group in the 5- or 8-position gives diazo-oxides which are intermediates for azo dyes. Thus 2-amino-5-naphthol-1,7-disulphonic acid dissolved in aq. NaOH is treated with benzenesulphonyl chloride to give the *O*-ester. Diazotisation followed by treatment with chlorine water at 30–40°c. gives the diazo-oxide—



Treatment with ammoniacal cuprous sulphate gives the copper-complex of the azo compound—



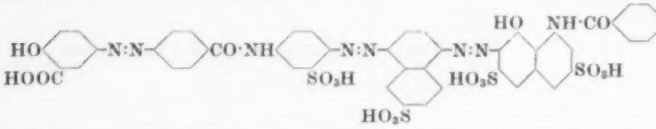
which dyes wool violet. E.S.

Anthraquinone Monoazo Pigments
General Aniline *USP* 2,884,410

The disulphuric acid ester of 2-amino-3-chloroanthraquinone is diazotised and coupled with an arylide of 3,2-hydroxynaphthoic acid, and the product is then hydrolysed and oxidised to give pigments for colouring fibre-forming polymers. Thus, using 3-hydroxy-2-naphtho-*o*-anisidide as the coupling component, the product is a red pigment. E.S.

Trisazo Direct Dyes for Aftercoppering or Diazotising and Coupling on the Fibre
Ciba *BP* 819,649

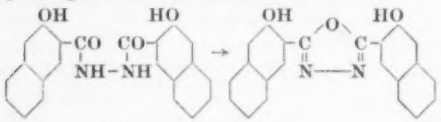
Diamines $H_2N{\cdot}R^1{\cdot}CO{\cdot}NH{\cdot}R^2{\cdot}NH_2$ (R^1, R^2 = *p*-phenylene residues) are tetrazotised and coupled with 1 mol. of a salicylic acid and then with a *p*-coupling primary amine. The aminodisazo compound so formed is then diazotised and coupled with a 1-acylamino-8-naphthol-3,6(or 4,6)-disulphonic acid, in which the acyl group may contain an NH_2 group, to give the title dyes. An example is—



which dyes cotton pure green, converted to yellowish green by diazotising on the fibre and coupling with 3-methyl-1-phenyl-5-pyrazolone. E.S.

Oxdiazoles—Coupling Components and Ultraviolet Radiation Absorbers
Ciba *BP* 817,096

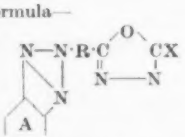
Diacyl hydrazines $R^1{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}R^2$ (R^1, R^2 = Ar of at most two 6-membered rings, at least one of which contains OH, preferably in *ortho* position to a –CO– group) are ring-closed by heating in a solvent with e.g. thionyl chloride to give the title products. Thus 2-naphthol-3-carboxylic acid hydrazide is heated in chlorobenzene with pyridine and 2-naphthol-3-carboxylic acid chloride, to give the dihydrazide. Heating in nitrobenzene with $AlCl_3$ then gives the oxdiazole thus—



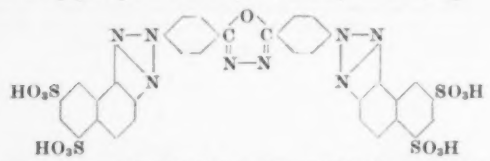
E.S.

Oxdiazole Fluorescent Brightening Agents
Ciba *BP* 821,843

Compounds of formula—



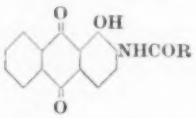
(X = a carbocyclic, heterocyclic or arylvinyl residue; R = a *p*-phenylene residue; A = an aryl residue) e.g.—



are fluorescent brightening agents suitable for application in a wide range of substrates by a variety of methods. The above compound is produced by slowly stirring the trisodium 4-[5′,7′-disulphonaphtho-1′,2′,4,5-triazolyl-(2)']-benzoate (52) into a solution of hydrazine sulphate (6·5) in oleum (190) while cooling so that the mixture never exceeds 30°c. The mixture is then raised in 30 min. to 65°c. and stirred for 8 hr. at 65–70°c. It is then allowed to cool, poured into ice water and neutralised with 30% aq. NaOH while cool to keep at < 30°c. The solution is then heated to 70–80°c., impurities filtered off and the product salted out with NaCl. C.O.C.

Monohydroxy-β-Acylaminoanthraquinone Disperse Dyes
Ciba *BP* 820,402

Yellow dyes for polyester, polyamide, and polyurethane fibres are—



(COR = residue of a monocarboxylic acid of 3–12 C). They are made by acylating 1-hydroxy-2-amino-anthraquinone with, e.g. propionic, isobutyric, lauric, benzoic, toluic, etc. acid. Solvents, e.g. nitrobenzene, chlorobenzene, and acid-binding agents, e.g. pyridine, are used. The products may be acid pasted after preparation and advantages in the dyeing of polyester fibres are obtained using mixtures of dyes of the formula shown, e.g. 1-oxy-2-aminoanthraquinone (12) heated in chlorobenzene (36) with dimethylaniline (6·6) and butyrylchloride (6) until there is no further change toward yellow yields a yellow disperse dye giving dyeings of excellent fastness to light and good fastness to sublimation on Terylene. E.T.

Polyhydroxy-β-Acylaminoanthraquinone Disperse Dyes
Ciba *BP* 820,448

Orange to bluish-red dyes for polyester, polyamide, and polyurethane fibres are anthraquinone derivatives containing (*a*) 2 hydroxyl groups in *α*-positions of one of the benzene rings and (*b*) in < 1 *β*-position, a primary amino group mono-acylated by a monocarboxylic acid residue of low to medium mol.wt. Anthraquinone starting materials are, e.g. 1,4-dihydroxy-2-amino-, 1,4,5-trihydroxy-2-amino-, 1,5,8-trihydroxy-2-amino-, 1,4,5,8-tetrahydroxy-2-amino-anthraquinones. Acids, e.g. acetic, caproic, hexahydrobenzoic, or their functional derivs. are used in inert organic solvents with acid-binding agents where necessary. E.T.

Halogenating Phthalocyanines
Ciba *BP* 821,629

Phthalocyanines, especially Cu phthalocyanine (C.I. 74160), are treated with a Friedel-Crafts compound and sulphur trioxide, anhydrous sulphuric acid or a compound of formula $R{\cdot}S{\cdot}O_3$ (R = OH, or –O–metal group or an organic residue). The process is particularly suitable for introducing 10–14 hydrogen atoms into the phthalocyanine. Thus anhydrous $AlCl_3$ (100), chlorosulphonic acid (50), NaCl (10) and NaF (1) are treated at 140–160°c. until a clean melt is obtained. To this is added at 140°c. Cu phthalocyanine (10), the mix stirred for 1 hr. at 140°c., for 2 hr. at 160°c. and then poured into ice water. The mixture is acidified with HCl, stirred for 1 hr. at 40–50°c. and filtered. The pigment filtered off is washed till neutral and dried. It is a pure green and contains 48–49% Cl. C.O.C.

Carbon Black (C.I. Pigment Black 6 and 7)
Godfrey L. Cabot *BP* 821,573

Modification of *BP* 819,823 (J.S.D.C., **75**, 546 (1959)). The aerosol resulting from the incomplete combustion of a hydrocarbon is shock cooled to < 1500°F. solely by an indirect heat exchanger placed in the stream of aerosol as it leaves the furnace. C.O.C.

Zinc Monoxy Chromates (C.I. 77955)
Orr's Zinc White *BP* 820,506

2 mol. of ZnO either as solid or as a boiling aqueous slurry are added to a boiling aqueous solution of 1 mol. of chromic acid. Formation of grits is much reduced by adding 0·1% Na citrate on the weight of the ZnO. C.O.C.

Aqueous Aluminium (C.I. Pigment Metal 1) (V p. 622)
Paints Pigmented with Iron Powder (V p. 622)
Relationship between Structure of Dyes and the Fastness of Dyeings (VIII p. 625)

Spectrum of Congo Red (C.I. Direct Red 28) in Cellophane, Poly(vinyl Alcohol), and Poly(vinyl Formal) Film (VIII p. 626)
Dyeing of Hydrophobic Fibres with α-Hydroxyanthraquinone Dyes (VIII p. 626)
Dyeing of Hydrophobic Fibres with 1-Amino-2-nitro-4-acylaminoanthraquinone Dyes (VIII p. 626)
Determination of Polymer Compositions in Dye Solutions by means of Absorption and Luminescence Centres (XIV p. 632)

V— PAINTS; ENAMELS; INKS

Flotation in Paints— A Suggested Mechanism

I. Ferguson

J. Oil and Col. Chem. Assocn., **42**, 529–542 (Aug. 1959)

The nature of solvent evaporation is the prime determinant of whether pigment migration to the air interface will take the form of flotation or flooding, but no pigment particles will be arrested at the air interface and no flotation or flooding will occur unless the pigment particles are in a suitable (probably relatively hydrophilic) condition. The situation will be aggravated and influenced by any factor contributing to pigment movement; this would include gravitational effects, secondary evaporation effects, and electrical effects. The prevention of pigment mobility, e.g. by induced thixotropy, results in reduced flotation. There are numerous photomicrographs. J.W.D.

Aspects of Pigment Finish Formulations

W. O. Nutt

J. Soc. Leather Trades Chem., **43**, 197–203 (June 1959)

The effect of pigment and other spacing matter on the properties of finish films is discussed and methods of controlling these properties are indicated. The formulation of finishes of known vol. content is described and procedures for making use of pigment vol. content and other factors in the production control of leather finishing are discussed. The effect of altering the charge of dispersed particles in pigment finishes is also discussed and methods for obtaining specific effects by means of charge control are considered. J.W.D.

Particle Size and Paint Manufacture

W. G. Wade

J. Oil and Col. Chem. Assocn., **42**, 548–556 (Aug. 1959)

A report of laboratory trials showing that very rapid dispersion, at least to ordinary gloss paint standards, can be effected with Micronized and similar pigments in dispersion-type mills in 4–20 min. The best method is to use the wetting power of the solvent and so to work in soln. of low resin solids content. Several types of mill are included in the study. J.W.D.

Effect of Particle Size Distribution of Pigment and Pigment Volume Concentration on Flat Wall Paint Properties (Solvent Type)

R. F. Hall *Off. Dig. Fed. Paint Varn. Prod. Cl.*, **31**, 788–799 (June 1959)

Particle size distribution of the pigments in a flat wall paint and the pigment volume concentration have a considerable effect on reflectance, hiding power, change in hiding on drying, tinting strength, colour uniformity, colour change on drying, and stain removal. There may be an optimal distribution of the particles that will produce the best compromise of properties, though other factors such as particle shape, surface treatment of the pigment particles, coalesced particles, and different binders, are also important. Good enamel hold-out, stain removal, and colour uniformity, do not necessarily go hand in hand; some other factor such as packing or correct particle size distribution may well determine whether the above properties are or are not good at the same time. It is tentatively suggested that rub-outs of pigment in oil cannot be used to predict behaviour in all vehicles (Contrast F. B. Stieg, *idem*— J.W.D.). J.W.D.

Relationship of Pigment Packing Patterns and Critical Pigment Volume Concentration to Film Characteristics and Hiding Power

F. B. Stieg *Off. Dig. Fed. Paint Varn. Prod. Cl.*, **31**, 736–751 (June 1959)

The relationship of pigment distribution in a paint film to hiding power below the "high dry hiding" level (at which the opacity of the dry film is boosted by the presence of interfaces of pigment, extender, and vehicle with air), and the relationship of the critical pigment volume concentration (CPVC) of a given pigment to its known particle size, are consistent with a uniform distribution of pigment in paint films in a rhombohedral pattern. Mathematical expressions of the CPVC concept are given for the prediction of wet-to-dry film shrinkage, film porosity, variation of hiding power with film porosity, and viscosity changes resulting from changes in extender. Other properties said to depend upon pigment packing patterns and void spaces are: resistance to blistering and to the rusting of metal finishes; enamel hold-out; ease of stain-removal; colour and sheen uniformity in flat wall paints. It is suggested that CPVC data determined by the spatula rub-out oil absorption method are of greater value in the control of these properties than average particle size data or distribution curves. J.W.D.

Size and Shape Properties of Representative White Hiding and Extender Pigments

A. C. Elm *Off. Dig. Fed. Paint Varn. Prod. Cl.*, **31**, 720–735 (June 1959)

The effect of the morphology and packing properties of particles of white pigments and extenders upon paint performance is discussed with the aid of ten electron micrographs. Combinations of pigments differing in particle size and shape may give rise to packing effects permitting the formulation of paints having excellent uniformity of hiding, colour, sheen, enamel hold-out, and other related paint properties. J.W.D.

Contributions of Pigments and Extenders to Organic Coatings

A. C. Zettlemoyer *Off. Dig. Fed. Paint Varn. Prod. Cl.*, **31**, 713–719 (June 1959)

A review, with particular reference to the wetting of solids (pigments and extenders), pigment dispersion, flow properties, optical properties of the film, and stability of the coating. Lines of potentially profitable research are indicated. J.W.D.

Fluorescent High-visibility Paints for Aircraft

J. S. Cowling and F. M. Noonan

Off. Dig. Fed. Paint Varn. Prod. Cl., **31**, Part 2, 1–19 (Aug. 1959)

Fluorescent paints of high visibility are widely used to minimise mid-air collisions between aircraft, and they can now be formulated so that they retain satisfactory colour and fluorescence characteristics for at least a year. A "high-visibility" colour has brilliance, good contrast with average backgrounds, and a colour lying within the region of max. sensitivity of the eye; a red-orange hue of dominant wavelength ca. 6110 A. provides the best compromise amongst these requirements. A fluorescent orange paint is shown to be greatly superior to the "international orange" non-fluorescent colour that has for long been in general use. The proper choice, specification, and formulation of colour for this purpose is discussed, and the spectral radiance of typical fluorescent aircraft finishes is compared with that of non-fluorescent finishes. These high-visibility colours are compared in lacquers and enamels. There are several spectral curves, a diagram of the fluorescence photometer used, and a glossary of terms. J.W.D.

Effect of Pigments on the Rate of Deterioration of Paint Films

P. Rosa and A. C. Elm

Off. Dig. Fed. Paint Varn. Prod. Cl., **31**, 1075–1085 (Aug. 1959)

There is evidence that paint vehicles, whether of oxidising type or not, suffer oxidative degradation on exposure to ultraviolet radiation. Long-oil alkyd, acrylic resin soln., and polyvinyl acetate soln. vehicles yield films that deteriorate at approx. the same rate. Zinc oxide inhibits this degradation the most strongly, though chalk-resistant titania has substantial effect; a small addition of ZnO to a TiO_2 paint has a disproportionately beneficial effect. J.W.D.

Stability of Aniline Printing Inks

T. K. Maher and E. W. Janssen *Adhäsion*, **2**, 83–8 (1959): *Chem. Abs.*, **53**, 16555 (10 Sept. 1959)

Agglomeration, sedimentation, and gelation of zein-containing printing inks can be retarded or prevented by addition of wetting agents. Of 49 such agents examined Tamol 731 and Amine 220 (2–2·5%) were most effective,

increasing the stability of non-modified inks from 10 weeks to more than 42 weeks. The reasons for the instability are discussed and comparative microphotographs of inks with and without wetting agent are given. C.O.C.

PATENTS

Aqueous Aluminium (C.I. Pigment Metal 1) Pastes
Eckart-Werke Standard Bronzepulver-Werke Carl Eckart *BP* 818,716

Aqueous or alcoholic solutions of carbohydrates and hexahydric alcohols are added to aluminium powder and the whole mixed with water. This yields a paste stable to oxidation of the aluminium and which is readily incorporated with aqueous or alcoholic media. Thus aluminium powder (40) is mixed with a carbohydrate (10) and hexahydric alcohol (10) in aqueous solution. The mixture is made into a paste by adding water or alcohol. The resulting paste can be made into a paint by mixing it with an aqueous binding agent. C.O.C.

Paints Pigmented with Iron Powder
National Research Development Corpn. *BP* 821,133

Paint, the pigment in which consists of at least 75% of iron powder, is suitable for direct application to iron or steel to protect it against corrosion, it being unnecessary to clean the surface before the paint is applied. Any vehicle may be used but plasticised polystyrene dissolved in xylene is preferable. C.O.C.

High Gloss Paint
General Electric Co. *USP* 2,890,192

Addition of a little of a tertiary amine to paints containing aromatic aldehyde condensates of the type described in *USP* 2,825,712, confers on them high gloss even when they are highly pigmented. C.O.C.

Light-fast Quinacridone Red Pigments (IV p. 617)

VI—FIBRES; YARNS; FABRICS

Chemistry and Structure of Textile Fibres
G. Centola *S.V.F. Fachorgan*, **14**, 242–253 (May 1959)

An explanatory paper describing in simple terms and with the aid of diagrams first principles of polymer chemistry of textile fibres. Examples are given of block and graft polymerisation and of atactic, isotactic, and syndiotactic steric forms of polymers. It is indicated how physical and chemical properties of textile fibres are determined by the structural characteristics of fibre-forming polymers. The author concludes by pointing out that fibre research is not only directed towards discovery and development of new synthetic fibres but also towards improvement of the natural fibres, e.g. cyanoethylation of cotton to render it resistant to the action of micro-organisms or halogenation of cellulose as a means of flameproofing. L.A.T.

Configuration of Fibres in Pleated Fabrics
H. W. Holdaway and V. Laws
Text. Research J., **29**, 496–499 (June 1959)

A description, illustrated with typical photomicrographs, is given of procedures and embedding media which have been used successfully to examine the microstructure of fabrics near pleats. S.B.D.

Distortions at a Wrinkle
M. J. Coplan and S. J. Golub
Text. Research J., **29**, 500–504 (June 1959)

A description and discussion, illustrated with photomicrographs, presented for the mounting and measuring the curvatures of fibres from a wrinkle. S.B.D.

Adsorption of Radioactive Sodiumcarboxymethylcellulose by Textile Fibres
J. W. Hensley and C. G. Inks
Text. Research J., **29**, 505–513 (June 1959)

Sodium carboxymethyl cellulose (CMC), labelled with C^{14} was used on cotton to investigate the relationship between adsorption and detergency action. Adsorption on cotton increased with increasing cation conc. and valency, the equilibrium adsorption in the presence of excess cations having a zero temperature coefficient. Detergency evaluations with labelled and unlabelled CMC showed that CMC adsorbed on cotton had a significant action in preventing redeposition of particulate soil materials. Measurement on other fibres indicated little or no adsorption of CMC by wool, Orlon, or acetate rayons. There was significant adsorption on nylon and rayon, but this could be greatly reduced by addition of an alkylaryl sulphonate. S.B.D.

Corval
S.V.F. Fachorgan, **14**, 253 (May 1959)

Corval, a new type of regenerated cellulose fibre launched recently by Courtaulds (Alabama, U.S.A.) has a number of interesting properties. Its water absorption, affinity for direct dyes and swelling properties are similar to those of cotton. It has a soft, wool-like handle and is admirably suitable for blends with synthetic fibres, particularly orlon. L.A.T.

***Aspergillus niger*— does it destroy Cellulose?**
M. Nopitsch and E. Möbus
Melliand Textilber., **40**, 677–680 (June 1959)

Tests with 7 races of *Aspergillus niger* of different provenance prove conclusively that this mould attacks cellulose, even when quite free from other fungi, although different races vary appreciably in cellulase production, and therefore in severity of attack. Cotton impregnated with a water-repellant generally showed lower strength loss. Although cotton with a starch dressing gave rise to more vigorous fungal growth, many races attacked the dressing preferentially, so that the samples were stronger than less overgrown unfinished ones. Linen tended to be attacked more vigorously, presumably because pectin-degrading enzymes are also produced. S.M.J.

Heat-induced Chemical Changes in Cotton Fibre
L. E. Hessler and H. Workman
Text. Research J., **29**, 487–492 (June 1959)

Cotton of various degrees of development were subjected to different amounts of heat in the laboratory, then submitted to a range of seven tests to determine if any changes had occurred. The data indicated that physical and chemical changes depended somewhat on the physical nature of the fibre. Physical tests were moisture regain, dye adsorption, and degree of swelling, the changes in these properties indicating structural changes in the fibre. Chemical tests were degree of nitration, D.P., carboxyl groups and carbonyl groups, the changes here also indicating structural changes in the fibre. S.B.D.

Changes in Crystalline Structure of Cellulose and Accompanying Phenomena
G. Centola *Melliand Textilber.*, **40**, 769–772 (July 1959)

The change in crystalline structure from cellulose I to cellulose II on mercerisation is irreversible because it is accompanied by a macromolecular change. X-Ray diffraction data provide evidence of increased lateral order, especially on ripening soda cellulose. These ribbon or lamellar structures are only evident in cellulose II, never in cellulose I, where they are latent. Untwisting of the less regular, spiralling macromolecule of cellulose I is facilitated by depolymerisation. Rotation of glucoside rings with chelate formation between the C3 hydroxyl groups and the oxygen of the neighbouring pyranose ring leads to flattening of the chain, engendering lamellae, and to a weakened lattice. If mercerisation is thus regarded as leading to decreased cohesion within crystallites, but increased cohesion between microfibrils, a better explanation can be provided for the otherwise apparently contradictory activation and passivation phenomena associated with the change. S.M.J.

Infrared Study of Oxidised Keratin
H. H. Stein and J. Guarnaccio
Text. Research J., **29**, 492–496 (June 1959)

An absorption band at 9·6 μ. was observed in the infrared spectra of oxidised human hair, callus, and wool, which was not present in the spectrum of the untreated materials. Although the nature of the group responsible for this new absorption band was not elucidated, it was established that absorption by keratin at 9·6 μ. was a specific test for a prior oxidative treatment. S.B.D.

Diffusion of Water into a Dry Keratin Fibre
M. Feughelman and M. S. M. Robinson
J. Applied Polymer Sci., **1**, 371–372 (May–June 1959)

The stress in a wool fibre held at fixed extension in water at 20°c. was measured by a strain gauge. It decays rapidly and after an hour reaches a constant value. If, at this stage, the water around the fibre is replaced by dry Analar glycerol, this gives an atmosphere effectively of

0% R.H.; the force rises rapidly and remains indefinitely at the value it reaches after a few minutes. The original force is recorded if the glycerol is afterwards replaced by water. Combined with previous results from experiments on torsional rigidity at different R.H., the present experiments confirm a two phase picture of the wool fibre: a water-impenetrable phase and a matrix which is accessible to water. Torsional rigidity depends almost entirely on the mechanical properties of the matrix; longitudinal force is the sum of the forces in each phase. P.T.S.

Alkali Solubility of Silk

P. Rochas and —. Pierret

Bull. Inst. Text. France, (78), 87–92 (Dec. 1958)

The method of Oku and Shimizu (*Textil Praxis*, **10**, 551 (1955)) has been applied to samples of silk degraded by chemical, photochemical, and thermal treatments. The results are compared with the fluidities of the samples in cuprammonium solution. Degradation by light or heat causes a rapid increase in alkali solubility and also an increase in fluidity. Degradation in acid solutions causes only a slight increase in alkali solubility. Degradation in alkaline or alkaline-oxidising solutions causes a slight decrease in alkali solubility, whereas the fluidity increases markedly. J.C.F.

Effect of Spherulites on the Mechanical Properties of Nylon-6,6

H. W. Starkweather and R. E. Brooks

J. Applied Polymer Sci., **1**, 236–239 (March–April 1959)

The presence of spherulites in nylon-6,6 increases the yield point and reduces the effects of variations in degree of crystallinity. Decreasing the size of the spherulites by providing more nuclei for their formation causes a higher flexural modulus and yield point, a lower ultimate elongation, and a loss of ductility. The effects are reduced by raising the temperature or water content. There is an analogy between spherulite size in nylon and grain size in metals. P.T.S.

Dynamic Mechanical Properties of Graft Copolymers of Nylon-6

Y. Shinohara *J. Applied Polymer Sci.*, **1**, 251–254 (March–April 1959)

A study of the dependence on temperature of the torsional rigidity and loss factor for graft copolymers of nylon-6 prepared by irradiation of the nylon filaments by γ-rays from Co^{60} in the vapour phase of vinyl monomer mixed with water. The presence of water increases the rate of graft copolymerisation considerably. P.T.S.

Dynamic Mechanical Properties of Nylon-6,6 and the Plasticising Effect of Water Vapour on Nylon—Part II

J. M. R. Quistwater and B. A. Dunell

J. Applied Polymer Sci., **1**, 267–271 (May–June 1959)

The dynamic tensile modulus and energy loss have been measured for nylon-6,6 monofilaments at 9 and 60°c. over a wide R.H. range using forced longitudinal vibrations. The energy loss arises from the motion of large polymer chain segments within the amorphous region of the nylon. Restraint of the motion of the chain segments is diminished by adsorbed water. The activation energy of the energy dissipation mechanism is estimated to be 60–80 kcal./mole. P.T.S.

Fine Structure of 6-Nylon Fibres and Phenol Absorption

H. Kanetsuna

II— The Swelling of 6-Nylon Fibres in Aqueous Phenol

J. Soc. Textile Cellulose Ind. Japan, **14**, 434–441 (July 1958)

The swelling is attributed to the absorption of phenol from solution. Initially, the absorption obeys Henry's Law, the phenol being taken up in the amorphous regions. With increasing phenol concentration, the less oriented of the crystalline regions become amorphous until above a certain concentration (0·04 g. phenol/g. water) the whole fibre is amorphous and the absorption again obeys Henry's Law. During the intermediate stages, the formation of highly crystalline regions can also occur, i.e. recrystallisation.

III— Estimation of the Lateral-order Distribution in 6-Nylon Fibres

Ibid., 442–446

The weight fraction (X_n) of the amorphous part of the fibre which swells in a phenol solution is given by $X_n = \frac{k_n}{K}$ where K is the partition coefficient between wholly amorphous 6-nylon and aqueous phenol and k_n is the partition coefficient between partly amorphous 6-nylon and aqueous phenol of concentration C_n. Plotting X_n against C_n and differentiating the curve gives the lateral order distribution for the sample.

By this method data are obtained for commercial 6-nylon fibres; dry heat-treated 6-nylon (170°c., 30 min.); aqueous heat-treated 6-nylon (145–150°c., 60 min.); and phenol-treated 6-nylon (40 g./l., 4 hr.) Histograms are given showing the lateral-order distributions. The effect of dry heat treatment is to decrease the amount of amorphous material and increase the amount of intermediate ordered regions. However, wet heat-treated fibres show fewer amorphous and more crystalline regions than commercial nylon, whilst the intermediate regions disappear. Phenol-treated 6-nylon fibres also show no intermediate regions, but the amounts of both the amorphous and crystalline regions increase. L.P.

Anionic Polymerisation of Lactams. III— Rapid Polymerisation of Oenanthic Lactam and *C*-Methyl-ε-Caprolactam

S. Schaaf *Faserforsch. und Textiltech.*, **10**, 328–330 (July 1959)

Alkaline polymerisation of the oenanthic lactam occurs more rapidly than that of the methyl-ε-caprolactam. Studies of the polymerisation of the latter permit conclusions to be drawn regarding the influence of a substituent on the alkaline polymerisation of caprolactams. W.R.M.

Ageing of Impregnated Glass Cloth containing Alkali

W. Bobeth and U. Renner

Faserforsch. und Textiltech., **10**, 263–270 (June 1959)

Ageing due to weathering causes a very rapid decrease of tensile and bending strengths and abrasion resistance. As ageing proceeds these appear to approach asymptotically values obtained in wet tests. Impregnating compounds only retard ageing. Heat-treated glass cloth shows less pronounced effects. W.R.M.

PATENTS

Cellulose Triacetate Yarn containing an Effect Material

BrC *BP* 821,431

The effect material, e.g. dye, pigment or flame-resisting agent, is dispersed in an acetate-soluble cellulose acetate which is then dissolved together with a much greater amount of cellulose triacetate in a suitable solvent, e.g. a mixture of methylene chloride with 6–14% by weight of methanol. This solution is then used to produce a yarn. C.O.C.

Fibres from a Mixture of Cellulose Acetate and an Acrylic Polymer

Eastman Kodak Co. *BP* 821,097

Fibres containing 70–95% by wt. of cellulose acetate and 30–5% of a copolymer obtained from a mixture of *NN*-dimethyl acrylamide and acrylamide, methacrylamide or *N*-methyl methacrylamide have excellent affinity for direct, disperse, vat, and wool dyes. C.O.C.

Coloured Polyamide and Polyester Fibres

ICI *BP* 820,975

A suspension of a heat- and solvent-stable phthalocyanine pigment in a water-miscible liquid aliphatic acid is added to a solution of a polyamide in the same or similar acid. The resulting suspension is diluted with water and the precipitate obtained is added to a polyester or polyamide before or after melting and before spinning the molten polyester or polyamide. Thus the β-form of Cu phthalocyanine (C.I. Pigment Blue 15) (100) in 95% formic acid (1000) is added to polyhexamethyleneadipamide (100) in 95% formic acid (700). The mixture is added to water (10,000) at 20°c. The precipitated pigmented polyamide is filtered off, washed with water (20,000), dried and ground. The powder (2) is mixed with nylon chips (100) which are then melted at 240°c. and formed into

filaments. The resulting yarn is a uniform blue of excellent fastness to light, washing, and dry heat.
C.O.C.

Tetrakis Hydroxymethyl Phosphonium Chloride as Colour Stabiliser for Acrylonitrile Polymers
Chemstrand Corpn. *USP* 2,889,303

Tetrakis hydroxymethyl phosphonium chloride prevents acrylonitrile polymers and their solutions from becoming discoloured upon prolonged heating or storage.
C.O.C.

Thermoplastic Threads
Dobeckmun Britain *BP* 821,149

A web or film has a pattern printed on it with a colorant and is then slit into narrow parallel strips suitable for use as yarns for weaving. The colorant is so applied that each strip has along its length areas on which there is colorant alternating with areas having no colorant. The web or film may be a single or a laminated structure and in the latter case the colorant, which may be a metal, may be between the layers.
C.O.C.

VII— DESIZING; SCOURING; CARBONISING; BLEACHING

Raw Wool Scouring
R. Keppler *Textil Praxis*, **14**, 568–575 (June 1959)

A literature survey of raw wool scouring (33 references) is followed by an account of an investigation into the effect of pH on the chemical modification of wool. Results of solubility of wool in alkali, acid, urea/bisulphite reagent, and staining with Methylene Blue and Sulphorhodamine B indicate that soap/soda ash scour is much more damaging than treatment in weakly alkaline non-ionic detergents.
L.A.T.

Soiling of "Wash and Wear" Textiles during Washing
F. Nestelberger *S.V.F. Fachorgan*, **14**, 287–289 (May 1959)

The author confirms the findings of earlier American workers that some "wash and wear" cotton textiles attract soiling matter from the wash liquor. Several types of proprietary synthetic resins, plasticisers, and water-repellent agents were tested, and it was concluded that polyacrylate and polysiloxane resins are, to a large extent, responsible for wet soiling during laundering. L.A.T.

Skin-fat in Textiles and its Removal
E. Walter *Melliand Textilber.*, **40**, 646–651 (June 1959)

Chromatograms of fresh and stale skin-fat demonstrate decrease in unsaturated fatty acid content, increase of unsaponifiable matter and resinification on ageing. Calcium soaps adsorb skin-fat and interfere with adsorption of fluorescent brightening agents. Synthetic detergents containing polymeric phosphates overcome this and, to some extent, iron contamination, and appeared more efficient than soap in removing skin-fat. Iron enhances resinification and causes yellowing above a threshold of 30 mg. per kg. skin-fat-containing textile. Iron free controls were not yellowed after 9 months' light exposure, unlike fabrics containing 44 mg. per kg. Fe after only 12 hr.
S.M.J.

Homologous Series of Surface-active Agents in Dry-cleaning
H. Wedell *Melliand Textilber.*, **40**, 798–801 (July 1959)

Artificially soiled wool is treated for 30 min. with tetrachlorethylene containing 4 g. per litre of surface-active agent. Degree of whiteness and foaming are measured. Air at 60% R.H., but no liquid water, is present and the dry-cleaning liquors are not filtered. Undesirable foaming is only exhibited by monoethanolammonium alkylbenzenesulphonates and sodium dialkylsulphosuccinates. Degrees of whiteness for the most effective members of the various anion-active series are: bleached wool 100, soiled wool 59, cleaned in tetrachlorethylene only 67·0, with triethanolammonium stearate 77·1, monoethanolammonium dodecylbenzenesulphonate 82·9, sodium dihexylsulphosuccinate 83·8. Nonionic alkylpolyglycol ethers have little effect, unless highly polymerised, e.g. $C_{18}H_{35}(OCH_2CH_2)_{40}OH$, 77·6, whereas polypropylene oxide has little effect. Sorbitol monostearate is beneficial (79·5) unlike the deleterious cation-active octadecylpyridinium chloride (63·0).
S.M.J.

Carbonising Investigations. VI— Surface-active Agents in Laboratory Carbonising
W. G. Crewther and T. A. Pressley *Text. Research J.*, **29**, 482–486 (June 1959)

Over 100 surface-active agents, mainly nonionic containing polyoxyethylene as the hydrophilic groups, but with a few anionic and cationic agents for comparative purposes, were tested to determine the extent to which they protect wool from loss of tensile strength during carbonising. Nonionic agents containing polyoxypropylene as the lipophilic portion gave little protection but when they contained alkyl or aryl hydrocarbon groups, the agents were generally effective. Cationic agents were comparable in their effects with the nonionic agents but the anionic agents were only effective when used at higher concentrations.
S.B.D.

Effect of Bleaching and Washing on the Elasticity of Knitted Textiles
H. Baier and E. Klass *Textil Praxis*, **14**, 607–610 (June 1959)

Elasticity is one of the most desirable properties of knitted goods. The investigations described by the authors have shown that the usual NaOCl, $NaClO_2$, and H_2O_2 bleaching treatments have no detrimental effect on the extensibility, but the elasticity decreases progressively on subsequent washing treatments.
L.A.T.

Chemical Bleaching Agents and Fluorescent Brightening Agents

I— M. S. Furry, P. L. Bensing, and J. L. Kirkley *Amer. Dyestuff Rep.*, **48**, 59–67 (20 April 1959)

Samples of a bleached and an unbleached cotton cloth were washed and dried repeatedly up to 50 times in a Launderometer for 15 min. at 60°c. per wash. Soap, with 0·06% optical bleach, or a domestic detergent (containing an optical bleach), each as 0·1% solutions, were used as washing agents both alone and with a range of added chemical bleaching agents (see below) at two levels and, in some cases, with added sodium sesquicarbonate. With the unbleached cloth, the chemical bleaching agents had a greater effect on total whiteness (fluorescent + nonfluorescent) than the optical bleach alone and those containing chlorine were the most effective while the peroxy compounds increased fluorescence. Similar, but less marked effects, were observed with the bleached cloth. Visual assessments of whiteness compared well with reflectance measurements. Repeated washing with soap or detergent had little effect on the fabric as judged by tensile strength and cuprammonium fluidity but the chemical bleaching agents caused damage which increased progressively according to whether the agent used was hydrogen peroxide, sodium percarbonate, dichlorodimethylhydantoin or sodium or calcium hypochlorite (24 references).

II— M. S. Furry, P. L. Bensing, R. K. Taube, N. D. Poole, and E. S. Ross *Ibid.*, 67–73

Pillowcases made from the bleached cotton fabric as used in Part I above were soiled in normal use and washed in a domestic washing machine together with samples of the unsoiled fabric. Soiling and washing were repeated 30 times. The domestic detergent (containing optical bleach) as in Part I was used together with sodium percarbonate (at two levels) and sodium sesquicarbonate as washing agent. Normal indoor and outdoor drying and heated tumbler driers were used. With indoor drying, results on the unsoiled test samples showed close correlation in reflectance (fluorescent and nonfluorescent) with the samples washed with the same agents in the Launderometer (Part I) but there was some evidence of greyness due to soil deposition on the test samples. Pillowcases washed with the lower level of percarbonate maintained their initial whiteness and at the higher level showed increased total (fluorescent + nonfluorescent) whiteness. Cuprammonium fluidity increased and tensile strength fell about 30%. Outdoor drying caused effective whitening but reduced fluorescence and led to a consistently higher cuprammonium fluidity than other drying methods. Wear accounted for about half of the increase in fluidity and the bleaching agent the remainder. Loss in tensile strength was 45%. Tumbler drying led to progressive yellowing.
E.C.

Bleaching of Fur Skins
M. Perlmutter *Rev. tech. ind. cuir*, **51**, 1–6 (1959): *Chem. Abs.*, **53**, 10817 (10 June 1959)

Discussion of the advantages of treating with HCHO to harden and improve the resistance to alkali of the hair. Bleaching with H_2O_2 preferably in alkaline medium in presence of stabilised $FeSO_4$ is dealt with. Surfactants give some protection to the hair during bleaching C.O.C.

PATENT

Bleaching Cellulosic and Synthetic Polymer Fibres
Bleachers' Assocn. *BP* 821,168

Use of an alkylene glycol polyester containing free carboxyl groups as the activating agent in chlorite bleaching enables lower temperatures to be used for bleaching. Thus 200 lb. of singed grey linen drill were batched on a stainless steel enclosed jig. The bath was made up of 40 gall. water, 8 lb. Na chlorite, 8 lb. Na nitrate (as corrosion inhibitor) and 4 lb. triethylene glycol succinic acid polyester (ratio 0·5 to 1) and acid value 250. The bath is brought to 80°C. and after 2 hr. running, the goods are transferred to another jig set with 40 gall. of water, 8 lb. NaOH, 4 lb. formaldehyde-sulphoxylate, 8 lb. soap and 4 lb. Lubrol W (ICI). The bath is raised to the boil and the goods worked in it for 1 hr. They are then washed with cold water and soured with 0·05*N* HCl. They are then run back into the first jig, the chlorite brought to the same strength and the goods worked in it for 2 hr. at 80°C. They are then transferred to another jig where they are first rinsed with cold water and then treated with an aqueous 0·5% solution of soap for 15 min. at the boil. The goods were a full white of good stability, had solubility about 4 and lost 8% in weight. This compares with a solubility of about 6 and a loss in weight of 17% usual with normal hypochlorite bleach. C.O.C.

Dyeing, Bleaching, and/or Waving of Hair (VIII p. 626)

VIII— DYEING

Optical Investigations into the Physical State of Dyes Adsorbed at Solid Surfaces
D. S. E. Campbell, D. Cathcart, C. H. Giles, and S. M. K. Rahman *Trans. Faraday Soc.*, **55**, 1631–1643 (Sept. 1959)

Spectrophotometric tests are made to determine whether dyes adsorbed in films of regenerated cellulose and gelatin are mono- or heterodisperse. Absorption spectra of Benzopurpurin 4B (C.I. 23500) in a number of solvents and adsorbed on solid films are described. There is evidence that the dye is partly monodisperse and partly aggregated in cellulose and still more aggregated in gelatin films. The effect of phenol on the extinction of certain dyes in aqueous solution and adsorbed in films can be correlated with its published effects as a dis-aggregating agent. The result is considered to be evidence for the presence of associated adsorbed dye. Tests of optical density against concentration relations for a variety of acid wool, metal-complex, direct cotton and disperse dyes in the presence and absence of a dis-aggregating agent suggests that most adsorbed dyes are present, at least partly, in aggregated form. W.R.M.

Relation between the Constitution of Neutral-dyeing Metal-complex Dyes, Distribution Equilibria between Liquid Phases, and Dyeing Equilibria on Polyamides
G. Back and H. Zollinger
Helv. chim. Acta, **42**, 1539–1553 (3 Aug. 1959)

The dyeing characteristics of a series of ten neutral dyeing 1,2-chromium and cobalt complexes of some *o,o'*-dihydroxy-monoazo dyes are reported. Partition between liquid phases (water/ethyl ether and water/ethyl acetate) and dyeing behaviour run parallel: one group is relatively hydrophobic and follows a solution mechanism in polyamide dyeing, whereas the other is less sol. in org. solvents and dyes polyamide fibres predominantly through a salt binding mechanism. Affinities are calc. for the salt binding mechanism of 6 dyes and 3 polyamides (nylon 66, 68, and 610) based on Remington and Gladdings' zwitterion model for polyamides (cf. *J.A.C.S.*, **72**, 2553 (1950)). In partition between an aq. buffer ($pH_{20°} = 6{\cdot}84$) and org. solvents it is the complex acid which is dissolved in the org. phase, whereas dyes form aggregates in the aq. phase. H.H.H.

Dyeing Mechanism of Neutral-dyeing Metal Complex Dyes
G. Back and H. Zollinger

II— The Solution Mechanism
Helv. chim. Acta, **42**, 1526–1538 (3 Aug. 1959)

The adsorption isotherms of a neutral-dyeing 1,2-chromium complex dye on nylon 66 indicate the dyeing process to consist of a competitive adsorption at the amino end-groups (salt binding mechanism) and a partition process (solution mechanism). The latter becomes predominant with increasing acidity and involves the undissociated dye acid since no sodium salts of the dyes are found to be adsorbed. Comparative isotherms on nylon 66, 68, and 610 show that the portion of the solution mechanism decreases from type 66 to 610 and becomes predominant on undrawn nylon 66. On a polyurethane and a dinitrophenylated nylon 66, a Freundlich-type isotherm results, whereas on *N*-ethyl nylon 66 the adsorption appears to follow a Nernst partition. The carbonamide groups of the polyamide fibre are essential for the solution mechanism.

III— Adsorption Isotherms on Natural Silk Wool and
Ibid., 1553–1557

The adsorption isotherms of two neutral dyeing 1,2-chromium complex dyes without ionised substituents have been obtained on wool, acetylated wool, and silk. In principle, the dyeing mechanism of these dyes on these fibres exhibits the same characteristics as on polyamides (cf. former papers) viz. the two processes of salt formation and a solution mechanism which proceed simultaneously; on wool, the latter is of minor importance. The calc. affinity of one of these dyes for wool via the salt binding mechanism (cf. *ibid.*, 1539–1553) is lower than its affinity for nylon 66. H.H.H.

Relationship between Structure of Dyes and the Fastness of Dyeings. I— Fastness on Wool of Acid Monoazo Dyes derived from Phenylazonaphthalene
B. I. Stepanov and M. V. Zakharova
Tekhnol. tekstil. prom., No. 1, (8), 148–157 (1959)

Introduction of ether groups into the molecule of acid azo dyes usually puts up the fastness to washing by 1–2 points. Alkoxy groups, including those having aromatic radicals at the end of aliphatic chains, have more effect on fastness than have aryloxy groups. The effect increases with increase in the number of C atoms in alkyl or alkylaryl radicals of the ether group, reaching the maximum at $\leqslant 8$ C. C.O.C.

Oxidation Potential of Vat Dye Solutions
M. S. Zakhar'evskiĭ, E. G. Musorok, K. M. Yakubov, and V. A. Lentovskaya
Vestnik Leningrad Univ., **14**, (4), *Ser. Fiz. i Khim.*, (1) 94–7 (1959): *Chem. Abs.*, **53**, 15817 (10 Sept. 1959)

Dependence of the oxidation potential (φ) on the relative concentrations of the unreduced and leuco vat dyes in solution plotted as (φ) *vs.* log. (C_{ox}/C_{red}) is linear with a somewhat smaller slope than the theoretical value. The unreduced dye in these solutions is colloidal. C.O.C.

Diffusion of Small Molecules in Semicrystalline Polymers— Water in Polyethylene
C. H. Klute
J. Applied Polymer Sci., **1**, 340–350 (May–June 1959)

A Study of Diffusion in Solids of Arbitrary Shape
H. A. Becker
J. Applied Polymer Sci., **1**, 212–226 (March–April 1959)

Relationship between Dichroism and Isotherm of Congo Red (C.I. Direct Red 28) sorbed in Vinylon and Regenerated Cellulose Fibre
K. Fujino, F. Fujimoto, and K. Fujita
J. Soc. Textile Cellulose Ind. Japan, **15**, 490–493 (June 1959)

The dye molecules orient with their long axis parallel to the polymer chains. The dichroic constant of a lightly coloured fibre differs from that of a deeply coloured fibre. A relationship between the amount of dye sorbed and the dichroic constant is based on the assumption that the sorption state in the fibre is partly of the Langmuir and partly of the partition type. With Vinylon this relationship agrees well with experimental data but for heat-treated poly(vinyl alcohol) fibre and regenerated cellulose the agreement is not good. C.O.C.

Spectrum of Congo Red (C.I. Direct Red 28) in Cellophane, Poly(vinyl Alcohol), and Poly(vinyl Formal) Film

K. Fujino and F. Fujimoto

J. Soc. Textile Cellulose Ind. Japan, **15**, 485–489 (June 1959)

In Cellophane the absorption maximum shifted to a longer wave-length (520 mμ.) than that of an aqueous solution of the dye. However, it shifted to the shorter wave-length (510 mμ.) as the amount of sorbed dye increased, first as the aggregation of dye molecules or ions is increased by increasing the amount of dye in the aqueous solution or by adding salt to it. With poly(vinyl alcohol) and poly(vinyl formal) films the absorption maximum bands appeared to be about 535 mμ. and 510 mμ. At lower dye concentrations the extinction coefficient at longer wave-length maximum was greater than that at shorter wave-length. At higher dye concentration this situation was reversed. When dyed film was stretched the extinction coefficient at longer wave-length maximum decreased, whereas that at the shorter wave-length increased. These phenomena are the same as the spectral behaviour of aqueous solutions of Rhodamine G (C.I. Basic Red 8) on change in concentration. The red shift of absorption maximum of Congo Red in polymer film resulted from association of the dye and polymer molecules (change of wave-length at absorption maximum depends on a n of substitute-solvation effect). The blue shift of absorption maximum or the increase in the extinction coefficient at lower wave-length maximum is caused by coagulation of the dye in the film. C.O.C.

Dyeing Synthetic Fibres with Vat Dyes— III

J. Müller *Melliand Textilber.*, **40**, 773–782 (July 1959)

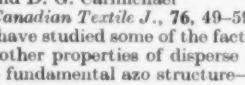
Polyester fabrics and blends with cellulose can be dyed continuously using the sequence pad–dry–thermosol process–reduction clear, and employing the range of 9 Polyestren (CFM) vat dyes, which have high light fastness, but are not suitable for deep tones. Thickening pad liquor with 1 g. of Solidocoll K (CFM) per litre prevents unevenness. 40–50 sec. at 190°C. are required for fixation of the 3 thioindigo derivatives, but 205°C. for the anthraquinonoid dyes. Solution of the pigments in the fibre is involved. Hot flues or pin-stenters are suitable for intermediate drying. The range can be adapted to pad-steam processing. Vat dyes suitable for filling in cotton are listed, as 4 of the range do not dye cotton under these conditions. It is also possible to dye polyester yarn packages with the vat acid, oxidise, and then thermosol process the final fabric, but whereas fixation increases up to 130°C., ease of oxidation decreases. S.M.J.

Constitution and Properties of Disperse Dyes

J. M. Straley and D. G. Carmichael

Canadian Textile J., **76**, 49–59 (1 May 1959)

The authors have studied some of the factors influencing the shade and other properties of disperse dyes, many of which have the fundamental azo structure—



Introduction of negative groups in *o*- and *p*-position to the azo linkage in ring 1 or positive groups in ring 2 cause a bathochromic shift. Fastness to light, washing, gas fume fading, and sublimation of 32 disperse dyes of known chemical constitution and in current use have been evaluated on the fibres on which they find the greatest use (cellulose acetate and triacetate, polyamide, and polyester). From the evidence available it may be concluded that, in general, fastness to light, washing, and sublimation on nylon is inferior to these properties on the other fibres. On cellulose triacetate the light, washing, and sublimation fastness of the dyes is, in general, about the same as on cellulose acetate. On polyester fibre the light fastness varies with the carrier used. Washing fastness is equal to or superior to that on cellulose rayon. The information should be of practical value, even though present knowledge does not permit a more scientific explanation of the facts. L.A.T.

Dyeing with Carbon Black

J. B. Donnet and D. Ferry

Teintex, **24**, 533–541 (Aug. 1959)

Carbon black, peptised by a special technique, fixes firmly to the surface of cellulosic fibres but with no penetration. The pores of viscose are concluded to have a mean diameter below 60 A. S.R.C.

PATENTS

Colouring Cellulosic Textiles with Reactive Dyes

ICI *BP* 820,470

Modification of *BP* 797,946 (J.S.D.C., **74**, 714 (1958)). Applying the acid-binding agent during treatment with the dye yields colorations of very good fastness to wet processing. Thus cotton cloth is padded with a 1% solution of the dye orthanilic acid→1-(4′,6′-dichloro-*s*-triazin-2′-ylamino)8-naphthol-3,6-disulphonic acid, 1% Na_2CO_3 and 0·2% of a highly sulphonated oil. It is then squeezed to a take-up of 200%, and dried in a stream of hot air at 110°C., rinsed and soaped. This yields a bright red dyeing fast to washing and light. C.O.C.

Dyeing Keratinous Fibres

Jos. H. Lowenstein & Sons *USP* 2,890,094

Keratinous fibres can be dyed at 20–57°C. if an unsaturated compound miscible with or soluble in water and ethanol is present in the bath. Thus undyed beaver skin was dyed for 90 min. at 40°C. in 1 litre of water containing Na_2SO_4 (5 g.), Ethofat C–15 (1), itaconic acid (50) thiourea (50), Anthraquinone Blue SWF (C.I. Acid Blue 25) (5), Calcocid Orange Y extra concentrate (C.I. Acid Orange 7) (1·5). The pH at the start was 1·9. This yields a good lustrous black, much deeper and more evenly dyed from the base to the tips and of much better lustre than another piece of the skin dyed in a similar solution from which the itaconic acid and thiourea had been omitted. C.O.C.

Dyeing, Bleaching, and/or Waving of Hair

P. de Gorter and A. Dalk *BP* 820,463

Oxidation of dyes, action of bleaching agents, and the neutralisation of setting lotions is accelerated and improved by treatment with ozonised steam during normal dyeing, bleaching or setting. C.O.C.

Continuously Dyeing Nylon with Acid Dyes

General Aniline *USP* 2,888,313

The nylon is passed through an aqueous dyebath at pH $\geqslant$ 7 and 175–212°F. containing 0·25–8·0 oz. per gallon (U.S.) and 2–16 oz. of a water-miscible, acid-stable, high boiling organic solvent for the dye. It is in the liquor for 20–90 sec. and after removal of excess liquor is steamed at 212–225°F. The whole process is continuous and yields heavy dyeings of good to excellent penetration, evenness and fastness properties. Thus nylon safety strap material is passed through a Williams unit containing a liquor containing per gallon (U.S.) 4 oz. Sulphon Cyanine 5RS (C.I. Acid Blue 113), 2 oz. Wool Fast Orange GA–CF (C.I. Mordant Orange 6), 1 oz. Anthralan Red BA–CF (C.I. Acid Red 42), 10 oz. *N*-methylpyrrolidone, 3 oz. NH_4 acetate. The liquor is at 200°F. The cloth is in contact with the liquor for 30 sec., is then immediately squeezed, continuously steamed for 3 min. at 215°F., rinsed and washed at the boil in a 0·1% aqueous solution of sodium-*N*-methyl-*N*-palmitoyl taurate. It is dyed a deep, level black of good penetration and good to excellent fastness to acid perspiration, alkaline perspiration, rubbing, and light C.O.C.

Dyeing of Hydrophobic Fibres with α-Hydroxyanthraquinone Dyes

Ciba *BP* 821,110

Yellow to red dyeings of excellent light fastness, good affinity and wool reserve are produced on polyester, polyamide, polyurethane, polyacrylonitrile, polyvinyl chloride or cellulose ester fibres using dispersions of α-hydroxyanthraquinone dyes which have in $\not<$ 1 β-position an alkoxy or phenoxy group. The alkoxy group may be aliph. or *cyclo*aliph. of 1–6 C and the alkoxy or phenoxy group may contain Hal or OH as substituents. Three examples are— anthraquinone nuclei containing the substituents (1) 1-hydroxy-2-methoxy, (2) 1,4-dihydroxy-2 phenoxy, and (3) 1,4,5,8-tetrahydroxy-2,6-dimethoxy. The dye in example (3) is made by alkylating the polyoxyanthraquinone, the β-groups only being alkylated. E.T.

Dyeing of Hydrophobic Fibres with 1-Amino-2-nitro-4-acylaminoanthraquinone Dyes

Ciba *BP* 821,111

Dyeings of excellent light fastness on hydrophobic fibres, e.g. Terylene, and cellulose esters are produced by using

dispersions of anthraquinone dyes containing the substituents 1-amino-2-nitro-4-acylamino. The acyl residue is of formula $-COC_nH_{2n+1}$ where $n \geq 5$. The dyes are made e.g. by monoacylating 1,4-diamino-2-nitroanthraquinone or by partially hydrolysing the diacyl derivative. E.T.

Dyeing Polyacrylonitrile, Polyester, and similar Fibres with Vat Dyes
General Aniline *USP* 2,890,092

The fibres are pad dyed in an aqueous bath containing a sulphuric acid ester of a leuco vat dye or a vat dye in free anthrol (acid vat) form and 5–20% by weight (of the dyebath) of an *N*-lower alkyl-2-pyrrolidone, e.g. *N*-methyl-2-pyrrolidone. C.O.C.

Dyeing Acrylic Fibres with Sulphur and Vat Dyes
General Aniline *USP* 2,890,093

The fibres are impregnated with an aqueous solution of the leuco dye at 205–220°F. in presence of 8–25% of sodium perborate on the weight of the fibres. Use of high pressure apparatus is unnecessary. The fibres must be saturated with the perborate before they come into contact with the leuco dye. The application of the perborate may be done at any desired temperature but dyeing must be done at 205–220°F. After dyeing, which usually takes 30–90 min., the fibres are oxidised in the normal way. If desired the perborate can be incorporated with the dye, the fibres then being treated with a dispersion of the dye before it is reduced so that dyeing may be carried out. C.O.C.

Sealing Dyeing Anodised Aluminium
8 *USP* 2,888,388

Addition to the conventional nickel acetate and/or cobalt acetate sealing bath of a lignosulphonate avoids formation of "smut" (deposit on heavily dyed aluminium of a reaction product of the dye, the aluminium oxide and the hot water). C.O.C.

Dyeing Properties of Acid Azo Dyes— III (IV p. 613)
"Tanning" and "Detanning" Action of Dyes (XII p. 630)
Polyampholyte with "Built-in Dye" (XIII p. 631)

IX— PRINTING

Printing Thickeners
W. Jülicher *Melliand Textilber.*, **40**, 655–657 (June 1959)

A discussion of the advantages in different applications of alginates, starch ethers, and other thickeners. S.M.J.

Vigoureux Printing Problems
R. Ruf *Melliand Textilber.*, **40**, 783–786 (July 1959)

With wool slubbing best results are obtained at or below pH 3, depending on the individual dye, in the presence of oxalic acid and of excess chromium fluoride as mordant. 2–3·5% of Detergyl S in the printing paste delays chroming, improves fixation, and definition. Preferred thickeners are British gum and carboxymethyl starch. Solanile Black F is suitable for viscose, 1:2 chrome complex dyes for Rilsan. Fastest results with polyester fibres are obtained using the Esterophile (Fran) dyes, which require steaming for 1 hr. at 140°C. S.M.J.

PATENTS

Duplicate Copies from Colour Negatives or Colour Positives
Agfa *BP* 820,730

Method for producing a duplicate copy from a subtractive multicolour transparency. C.O.C.

Resin-coated Metal Foil Printed Appliqué
E. A. Steffey *USP* 2,889,233

A multi-colour printed appliqué has aluminium foil coated with a resin as the backing, the design being printed on the resin film with an ink based on a resin compatible with the resin film and a strong solvent for the film. C.O.C.

Deposition of Inks, Paints, and other Viscous Liquids— Multicolour Printing in One Operation (I p. 612)

X— SIZING AND FINISHING

Improvement of the Light Resistance of Nylon III— Reactions of the Amino End-groups of Nylon with Monofunctional Reagents
T. Hashimoto
J. Soc. Textile Cellulose Ind. Japan, **14**, 484–489 (July 1958)

The reactions of nylon with aldehydes, acid anhydrides, acid chlorides, nitrous acid, isocyanates, acrylonitrile and acrylic esters are investigated, and the resistance of the nylon to tendering by light after reaction is measured. Reaction with the amino end-group does not necessarily improve the light fastness, but acetic anhydride, phenyl isocyanate, acrylonitrile, and acrylic esters give marked improvement. L.P.

Setting of Perlon Filament
H. Sauer and E. Glausch
Faserforsch. und Textiltech., **10**, 260–263 (June 1959)

Studies of the effects of variations in temperature and time of setting and in the tension of the fibres are reported. Variations in time of setting have little effect once a certain minimum time is exceeded. Little variation in temperature is permissible. Variations in tension may cause considerable change in properties and there is a rough proportionality between certain properties and tension in the range 0 to 0·3 g./denier. W.R.M.

Chlorine Retention of Dimethylolethyleneurea Resins on Cotton
A. R. Smith
Amer. Dyestuff Rep., **48**, 49–53 and 58 (20 April 1959)

Samples of 3¼ oz. cotton fabric were treated with a dimethylolethyleneurea resin using different curing catalysts and temperatures with and without final washing-off and were then examined for degree of cure by loss in total nitrogen content on soaping 10 min. at 95°C. Chlorine retention of treated samples was tested by a modified AATCC method in which, after immersion in hypochlorite solution (0·25% available chlorine) a scorch test at 200°C. for 30 sec. was applied followed by the usual tensile strength tests. Unbleached samples were included as controls. Tests were applied to the resin-treated samples with and without washing-off and before and after mild and severe washing, normal storage and an accelerated storage procedure. Results reported in detail lead to the conclusions that zinc nitrate hexahydrate (at 12% on resin solids) and magnesium chloride (at 5% on resin solids) are satisfactory curing catalysts (ammonium salts and organic acids are not) but that a degree of cure > 95% is only achieved if the curing temperature is 160°C. This high degree of cure is essential, as also is adequate washing-off immediately after curing, if the treated fabric is to remain free from chlorine retention on washing in presence of sodium hypochlorite after storage. Since, theoretically, a fully cured dimethylolethyleneurea resin contains only fully substituted nitrogen atoms it should be inert to sodium hypochlorite. Catalyst residues not washed off from the treated fabric can during storage promote degradation of ether linkages especially those which may arise from self condensation of the resin rather than its condensation with cellulose, to reform the original methylol groups. At this stage the fabric is still free from chlorine retention but on severe washing it is postulated that loss of formaldehyde occurs with the formation of s-amino groups and hence development of chlorine retention. Recuring of an inadequately treated fabric after storage is shown to appreciably reduce its chlorine retention. E.C.

Fireproofing of Cotton
C. Weimann *Teintex*, **24**, 483–486 (July 1959)

A discussion of the work of Ponomarenko (*Tekstil. prom.*, **19**, 69–71 (Jan. 1959)) with recipes. S.R.C.

Reaction of Wool Cystine with Sulphite
G. Gianola and R. Grillot
Compt. rend., **248**, 2101–2102 (1959): *Chem. Abs.*, **53**, 15575 (25 Aug. 1959)

When wool is treated with bisulphite about half the cystine has its disulphide bonds broken; under severe conditions of strength, temperature, and time, the remainder of the cystine is decomposed into α-amino acrylic acid (I). Treatment of purified fibres with 0·3M-sulphite for 30 min. at 60°C., followed by rinsing in distilled water, gives rise to some cysteic acid (II) not initially present in the

HCl hydrolysate of the wool. II, normally an oxidation product from wool, is not formed by heating wool under the same conditions with 0·1 N-Na_2CO_3 and is not, therefore, formed by a secondary reaction of atmospheric O in alkaline medium. II therefore results from addition of 1 mol. of sulphite on the double bond of the I in the wool. This is confirmed by the fact that in wool treated for 30 min. at 100°C. with Na_2CO_3 buffered at pH 10, a significant fraction of the cystine is converted to I; paper chromatography shows that if the fibres are subsequently boiled in sulphite solution an increased amount of II is formed; this indicates the rôle of I in this reaction. C.O.C.

Metallising of Flexible Substrates
P. J. Clough
Nat. Symposium on Vacuum Technol., 4th., Boston, **1957**, 136–137 (Publd. 1958)

For metallising sheet materials, e.g. paper, textiles, plastics, economy demands that the operation be performed on rolled stock. Problems encountered by using Al as the liquid metal are discussed, as > 1200°C. Al is an extremely active solvent. A technique has been developed which enables use of C-base crucibles and makes possible evaporation of Al at high, steady rates for hours on end. The technique involves addition of Zr to the molten Al. The Zr forms ZrC, insoluble in Al and of > d., which precipitates out on the C wall supporting the melt and forms a lining which protects the C from the molten Al. C.O.C.

Polyethylene Oxide in Aqueous Solution
F. E. Bailey and R. W. Callard
J. Applied Polymer Sci., **1**, 56–62 (Jan.–Feb. 1959)

An interpretation of the rheology of aqueous solutions of ethylene oxide polymers. P.T.S.

Finishing Perlon Charmeuse
G. Troeltzsch *Melliand Textilber.*, **40**, 665–670 (June 1959)

A discussion of practical processes for dyeing and finishing Perlon Charmeuse. Some of the points emphasised are: rapid cooling after dry thermofixation; danger of degradation on incomplete removal of oxygen before steam-setting; suitability of hypochlorite-peroxide as well as of chlorite bleaching; high temperature dyeing; and the Swedish Krumpex shrinkage process, which obviates subsequent washing shrinkage. S.M.J.

Finishing Knitted Fabrics
W. Ernst *Melliand Textilber.*, **40**, 793–798 (July 1959)

A summary of recent developments dealing with products, processes, machinery, and testing methods. S.M.J.

PATENTS

Finish for Sewing Thread
American Thread Co. *USP* 2,888,365

The thread is coated first with a pressure sensitive-adhesive, e.g. the polyvinylether derivative sold by Angier Products as No. P.S.M. 271–1, and then, after removal of the solvent, with microcrystalline wax. The treated thread when cross-wound into a bobbin and compressed at normal temperature is held together by the correct degree of tack so that it is part of the mass up to the moment it is drawn away. This ensures that when the bobbin is used in a sewing machine the unwound portion of the bobbin retains its shape and the thread is withdrawn in a free even flow so that even stitching results. C.O.C.

Decreasing the Water Imbibition of Regenerated Cellulose Fibres
Courtaulds *USP* 2,888,369

When applying resin finishes presence of a water-soluble ketone, e.g. acetone, results in a product far less brittle, of better handle and more easily processed than if treated with the resin alone. The ketone may be added to the resin liquor or may be applied to the fibres before or after the resin but before curing. C.O.C.

Crease-shedding and Dimensionally-stable Finish for Cellulose Textiles
American Cyanamid Co. *USP* 2,889,192

The material is treated with a diester of formula—

$$R{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}(O{\cdot}[CH_2]_m)_n{\cdot}(O{\cdot}CH_2)_p{\cdot}O{\cdot}CO{\cdot}R$$

(R = H or Alk; $n \not< 0$; $m > 0$; $p = 1$ but may = 0 when $n = 0$) and an acid catalyst and then baked. The treated material loses little in tensile strength when scorched following chlorine bleaching nor does it discolour after repeated chlorine bleaching. Aminoplast resin precondensates can be added to the bath if desired. Thus cotton percale was impregnated with its own weight of a bath containing 5·15% of ethylene bis(oxymethylene) diacetate and 2·9% $MgCl_2$, dried for 2 min. at 210°F. and baked for 2 min. at 300°F. The treated fabric had excellent crease shedding properties. C.O.C.

Cellulose Materials Having Self-sterilising and Bactericidal Properties
ICI *BP* 821,113

Impregnating cellulosic material with 0·001% of its dry weight of a bis-guanide of formula—

$$A{\cdot}X{\cdot}NR{\cdot}\underset{\underset{NH}{\|}}{C}{\cdot}NH{\cdot}\underset{\underset{NH}{\|}}{C}{\cdot}NH{\cdot}(CH_2)_n{\cdot}NH{\cdot}\underset{\underset{NH}{\|}}{C}{\cdot}NH{\cdot}\underset{\underset{NH}{\|}}{C}{\cdot}NR{\cdot}X{\cdot}A$$

(A = phenyl which may be substituted by Alk, alkoxy, NO_2 or Hal; X = a direct link or alkylene of < 4 C; R = H, Alk or aralkyl; $n = 2$–12; the $(CH_2)_n$ chain may be interrupted by O atoms and/or aromatic nuclei), e.g. 1,6-di-(N_1,N_1'-*p*-chlorophenylbiguanido-N_5,N_5') hexane, renders itself sterilising and bactericidal. The finish is fast to washing being suitable, e.g. for surgical towelling. C.O.C.

Protecting Cellulosic Fibrous Materials of Low Swelling Capacity from Attack by Micro-organisms
Ciba *BP* 820,946

Modification of *BP* 745,638 (J.S.D.C., **72**, 310 (1956)). Fixation is carried out simply and more quickly by using steam as the source of heat instead of hot air. Cross-wound packages are heated throughout by this means in a short time even in the innermost layers. By using saturated steam there is no risk of local drying out. By working at high temperatures, e.g. 110–140°C., the time of fixation can be so much reduced that the whole process, including heating up, can be completed in 1–2 hr. C.O.C.

Reducing the Tendency of Wool to Felt and Shrink
Finishing Processes (Textiles) *BP* 821,135

The material is first treated with a dispersion of a synthetic resin containing a cationic dispersing agent at pH < 7 and then with a halogenating agent at pH < 7. Thus water (300 gall.) at 70–75°F. was placed in a paddle dyeing machine and brought to pH 5 with formic acid. An aqueous dispersion (1 lb.) of poly(methyl methacrylate) plasticised with dibutyl phthalate (32–34% of total solids of which the plasticiser is 40%) and containing cetyl pyridinium bromide as dispersing agent and a nonionic dispersing agent was added. Wool half-hose (100 lb.) previously scoured with a nonionic detergent and brought to pH 5 with formic acid, were then placed in the liquor and worked in it for 15 min. This completely exhausted the plasticised polymer on to the goods. They were then lifted out and placed in a fresh aqueous bath of such volume that addition of 8·5 pints commercial NaOCl gave 2% available chlorine on the weight of wool, the bath being brought to pH 5 with formic acid. The goods were treated in this bath for 15 min. and then in the same bath with Na_2SO_3 (10 lb.) to clear remaining chlorine, and rinsed. C.O.C.

Rendering Textiles Dimensionally Stable
U.S. Secretary of Agriculture *USP* 2,890,097

The textile is impregnated with a polyamide and then treated with a vaporised polyepoxide. This yields a product which is virtually shrinkproof in normal laundering while the handle, colour, resiliency, porosity, tensile strength, and other valuable properties are retained. The treated material has also much improved crease shedding properties. The process is particularly applicable to wool textiles. Thus white wool cloth impregnated with an aqueous emulsion of a polyamide, is dried and then exposed to butadiene dioxide vapour for 72 hr. at room temperature. The treated fabric had very good dimensional stability to washing. C.O.C.

Preventing Yellowing of Wool on Exposure to Light
U.S. Secretary of Agriculture *USP* 2,888,315

Wool is protected against ultraviolet radiation by treating it with a boiling aqueous solution of a compound of formula—

(R = alk; n = 1 or 2) e.g. 2-hydroxy-4-methoxybenzophenone-5-sulphonic acid, 2,2′-dihydroxy-4-methoxybenzophenone-5-sulphonic acid and 2,2′-dihydroxy-4,4′-dimethoxybenzophenone-5-sulphonic acid. C.O.C.

Non-slip Finish for Nylon Yarns
Inventa A.G. für Forschung und Patentverwertung
BP 821,266

The yarn is treated with a dispersion of a polyamide in a polyamide adhesive, e.g. an 8% methanol solution of a resorcinol–propionic aldehyde adhesive containing in suspension 13·5% of a mixed polyamide consisting of 60% nylon and 4% caprolactam of average particle size 30 μ. C.O.C.

Dyeing, Bleaching and/or Waving of Hair (VIII p. 626)

XI— PAPER AND OTHER CELLULOSIC PRODUCTS

Oxidation of Cellulose with Nitrogen Dioxide
H. Demus
Faserforsch. und Textiltech., **10**, 319–327 (July 1959)

The reaction of cellulose and nitrogen dioxide is exothermal because of sorption and nitric acid formation. Sorption can be regarded as pressure- and temperature-dependent swelling. Strong swelling makes the cellulose more accessible allowing subsequent reactions to occur more rapidly. A continuous preparation of celluronic acid is outlined. The sorption conditions have a considerable influence on the properties of the celluronic acid. 78 references are given. W.R.M.

Softener Absorption by Regenerated Cellulose. Uptake from 10% Aqueous Glycerol
O. J. Sweeting, R. Mykolajewycz, E. Wellisch, and R. N. Lewis
J. Applied Polymer Sci., **1**, 356–360 (May–1959)

The softener content of regenerated viscose cellulose film in equilibrium with aqueous glycerol solution is determined by the softener concentration in the solution and the free space within the film. At the softener concentrations studied the free volume of the film is not altered by softener uptake. P.T.S.

Ball-milling of Cellulose Fibres and Recrystallisation Effects
J. A. Howsmon and R. H. Marchessault
J. Applied Polymer Sci., **1**, 313–322 (May–June 1959)

The rate of decrystallisation of cellulose when ball-milled depends on the original fine structure and it is accelerated by the presence of moisture. The chain degradation is greater in an oxygen atmosphere than in a carbon dioxide atmosphere, thus suggesting that radicals are produced during the milling. There is a linear relation between the moisture regain and the density of the samples after various times of milling. The type of lattice which recrystallises after ball-milling depends on the original lattice, the extent of milling and the conditions of recrystallisation, and a highly ball-milled sample can be made to recrystallise either as cellulose I, II, or IV. P.T.S.

Force–Temperature Behaviour of Swollen Cellulose Model Filaments
E. Passaglia and H. P. Koppehele
J. Applied Polymer Sci., **1**, 28–36 (Jan.–Feb. 1959)

A viscose solution was spun from a burette into an ammonium sulphate coagulating bath. Some of the fibres were left isotropic (not stretched), others were extended 20, 40, 60, 80, 100% when freshly regenerated and allowed to dry at constant length. The densities and orientations of the filaments were measured. The fibres were in turn held at constant length in water at various temperatures, and the force necessary to hold the filaments at constant length was plotted against the temperature of the water. The force–temperature curve shows a maximum; the temperature of the maximum decreases with increasing orientation of the fibre. Theoretical interpretation of the results is difficult. P.T.S.

Water and Ion Flow across Cellulosic Membranes
C. E. Reid and E. J. Breton
J. Applied Polymer Sci., **1**, 133–143 (March–April 1959)

Ions and molecules which cannot enter into hydrogen bonding with cellulose acetate are transferred through a cellulose acetate membrane by a hole type diffusion. Ions and molecules which can form hydrogen bonds with the membrane are transferred by an alignment type diffusion. The latter type is favoured by compressing the membrane which decreases the hole type diffusion. The experiments were carried out in an attempt to find a feasible method of removing salt from sea water. The electrical resistance of specific ions across cellulose acetate membranes was measured. P.T.S.

Dielectric Studies on Cellulose Fibres
Yoichi Ishida, Masatsugu Yoshino, and Motowo Takayanagi
J. Applied Polymer Sci., **1**, 227–239 (March–April 1959)

A method of obtaining the intrinsic dielectric constant and loss factor of dry cellulose fibre (viscose rayon, cuprammonium rayon, cotton sliver) along the fibre length is described. The results suggest that dipoles in the amorphous region of cellulose and on the surface of the crystallites provide the chief contribution to the dielectric dispersion and that there is a secondary transition point associated with these dipoles at −20°c. P.T.S.

Formation of 1,6-Anhydroglucofuranose in the Thermal Decomposition of Cellulose
O. P. Golova, N. M. Merlis, and Z. V. Volodina
Zhur. obshch. khim., **29**, 997–1000 (March 1959)

It is shown that the thermal decomposition of cellulose (CE) under a vacuum leads to the formation of 1,6-anhydroglucofuranose (3% on the wt. of CE). G.J.K.

PATENTS

Water-resistant and Water-repellent Paper Coatings
S. D. Warren Co. *BP* 816,679

High gloss and water resistance are obtained when paper is coated with a composition consisting of a dispersion of pigment or filler together with a protein adhesive, e.g. casein or soya protein, in an ammoniacal soln. of a chelate complex of Al, Fe, Cr or Sn. During drying and super-calendering the protein combines with released multivalent ions giving a water-resistant or even hydrophobic coating. R.A.

Paper to be printed with High-gloss Oil Inks
American Cyanamid Co. *USP* 2,889,299

The covering power of anionic emulsions containing flexible hydrophobic thermoplastic linear polymers can be extended without decrease in the grease-resistant finish they impart to paper, by incorporating in the emulsion a hydrophobic inorganic material of particle size within the pigmentary range, i.e. 0·2–1·0 μ., e.g. TiO_2, $CaCO_3$, Mica, Talc, and Kaolin (C.I. Pigment White 6, 18, 20, 26, and 19). C.O.C.

Bleaching of Fur Skins (VII p. 625)
"Denaturation" of a Synthetic Polyampholyte (XIII p. 630)

XII— LEATHER; FURS; OTHER PROTEIN MATERIALS

Effects of Gamma Radiation on Collagen
J. Cassel
J. Amer. Leather Chem. Assocn., **54**, 432–451 (Aug. 1959)

Absorption of gamma radiation by collagen as a purified powder or as kangaroo tail tendon, produces a drastic decrease in shrinkage temp. and an increase in water-soluble material. The decrease in shrinkage temp. is the same in air or *in vacuo* and, in the case of the tendon, was not influenced by moisture content. Relatively little damage to amino acid structure occurs with absorption doses of < 20 megarads. After a dosage of 225 megarads only 73% of the amino acid structure was recoverable by analysis. The amino acid components most susceptible to alteration by radiation are: methionine, phenylalanine, and threonine. Alanine, glycine, hydroxyproline, proline, and arginine, are the least affected. Radiation causes a non-hydrolytic type of peptide chain scission. Increased ultraviolet absorbance by the water-soluble fractions is attributed to the formation of complex ultraviolet-absorbing groups, rather than to light-scattering resulting from particle agglomeration. J.W.D.

Hot-water Fractionation of 2,4-Dinitrophenylcollagen
C. Deasey
J. Amer. Leather Chem. Assocn., **54**, 503–514 (Sept. 1959)

Fibrous collagen of bovine corium which has been purified by extractions with NaCl, phosphate, and citrate

soln. differs on histological examination from fibrous collagen of the same origin extracted with NaCl soln. only. The 2,4-dinitrophenyl (DNP) derivatives of the two collagen preparations differ also in hot-water solubility, in the paper-electrophoretic patterns of their hot-water-sol. fractions, and in the number of N-terminal amino acids present in their hot-water-sol. fractions. Both the sol. and insol. fractions of the two DNP collagen preparations have essentially the same ratio of N to hydroxyproline. The insol. fractions of both preparations form on hydrolysis a DNP cpd. which appears to be of carbohydrate character and related to sialic acid. J.W.D.

Reaction between Collagen and Polyfunctional Epoxides

R. L. Sykes *Chem. and Ind.*, (23), 700–701 (6 June 1959)

Measurements of the increase in shrinkage temp. of purified skin collagen show that cross-linking occurs only with di- and tri-epoxides, and that reaction is favoured by high pH. *O*- and *N*-acetylation has the greatest effect in reducing the amount of cross-linking, suggesting that the OH residues of hydroxyproline, serine, and threonine are involved in the reaction between epoxides and collagen. Deamination and esterification have only slight effect on the extent of cross-linking. It is suggested that the differences in the cross-linking activity of the three polyepoxides investigated, can be ascribed to the spatial orientation of the epoxide groups in the molecule, limiting their ability to react with the relatively immobile side-chains of a fibrous protein. J.W.D.

Occurrence of 'Ester-like' Linkages in Collagen

P. M. Gallop, S. Seifter, and E. Meilman

Nature, **183**, 1659–1661 (13 June 1959)

Experimental evidence is given of the cleavage of various kinds of gelatin by either hydroxylamine or hydrazine under conditions favouring the disruption of ester bonds. The reactions occur without the concomitant splitting of peptide bonds, yielding non-dialysable proteins of ca. 20,000 mol.wt. which react in the one case as hydroxamides and in the other as acid hydrazides. J.W.D.

Synthetic Resin Dispersions for Leather Finishing

J. A. Handscomb

J. Soc. Leather Trades Chem., **43**, 237–255 (July 1959)

Properties of ten acrylic and vinyl resin dispersions are reviewed and compared in both pigmented and unpigmented films. Finishes based on these dispersions were applied to leathers which were then tested for wet-rub fastness, dry-rub and scuff resistance, adhesion, flexibility, plating tack, gloss, grain break, handle, resistance to water spotting, resistance to solvents, barrier properties under nitrocellulose finishes, and ageing; the methods used are fully described. Butadiene–methyl methacrylate copolymer dispersion, though not ideal, gives good properties for many purposes, at low cost. J.W.D.

Waterproofing Leather

F. R. Morgan

J. Soc. Leather Trades Chem., **43**, 312–319 (Sept. 1959)

The waterproofness of leather may arise from several factors and it cannot be characterised fully by any single test; test methods in common use are reviewed. There is as yet no successful means of waterproofing vegetable-tanned leathers by treating the fibre surfaces, and methods designed to fill the capillary spaces must be used. Fibre-surface treatments are successful with most chrome-tanned leathers but, although ~1% of proofing agent is sufficient to coat completely all the fibre surfaces with a very thin film, about 10% is in fact necessary for effective protection. A cheap and effective method is still needed. J.W.D.

"Tanning" and "Detanning" Action of Dyes

G. Otto *Rev. Tech. Inds. Cuir*, **51**, 197–203 (1958)

Some leather dyes cause appreciable modification of the quality of the leather but the effect in different tanneries may differ. It is not caused by overneutralising the leather. Some dyes have a tanning action as would be expected because their structure is similar to that of the syntans. They have chains of conjugated double bonds and the affinity of a syntan or dye for chrome leather increases with length of that chain. Dyes having a tanning action and mol.wt. > 350 improve the quality of the leather if the grain is not overtanned and absorptivity of the leather is not increased so much that finishing becomes difficult. Instead of exerting a tanning action other dyes of lower mol.wt. may form soluble compounds with Cr salts and thus may partly detan chrome leather. Where dye mixtures are used both effects may be present. Dyes can enter the Cr complex and their action may be modified by masking agents. Freshly precipitated $Cr(OH)_3$ was treated with four dyes of varying astringency and with masking agents. Formate, a weak masking agent, did not prevent take up of dye or displace dye from dyed $Cr(OH)_3$. The strong masking agents, phthalate, oxalate, and hexametaphosphate, prevented take up of dyes or displaced them. Citrate, adipate, malonate, and sulphophthalates were intermediate in action and displaced only the less astringent dyes. The undesirable effects of dyes on leather quality can be avoided by use, preferably during neutralisation, of a masking salt with medium affinity for Cr. If the dye detans too much, it may be overcome by use of 60% basic $AlCl_3$ either during fixation of the dye or in the final stages of tanning. C.O.C.

XIII—RUBBER; RESINS; PLASTICS

"Denaturation" of a Synthetic Polyampholyte

M. L. Bhaskara Rao and S. R. Palit

Proc. Chem. Soc., 222 (Aug. 1959)

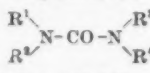
A copolymer (I) of aminostyrene and methacrylic acid is found to exhibit behaviour similar to the denaturation of native proteins. It has a wt.-average mol.wt. of 3×10^5, is almost neutral, and has carboxy- and amino-groups in almost equal proportions, about two-thirds of the former being present as Na salt. Its soln. on acidification with HCl to below pH 3 remains clear for a long time and then the whole polymer is suddenly thrown out of soln. When freshly pptd., the polymer easily redissolves in alkali but becomes increasingly insol. with time, an insolubilisation which occurs stepwise, the first step being irreversible. Time of pptn. decreases with temp. increase, and its reciprocal is almost proportional to the acid concn. The reaction appears to be that of slow replacement of some bound Na by H with pptn. when a definite fraction is replaced; it is unimol. with respect to I and bimol. with respect to H^+ concn. and its mechanism seems to comprise two steps, viz. ..CO_2 Na..CO_2^-..$+H^+ \rightleftharpoons$ ..CO_2Na..CO_2H..(1) and ..CO_2Na..CO_2H..$+H^+ \rightarrow$..CO_2H CO_2H.. (2), where (1) is a rapidly attained equilibrium and is displaced to the left, while (2) is a slow reaction. The analogy with pptn. of proteins extends to the effect of org. solvents, e.g. alcohol and acetone, viz. pptn. after a time-lag and show insolubilisation as with addition of acid and also with similar temp. effects. Evaporating the soln. and drying the ampholyte renders the residue insol. in acid and alkali, and X-ray examination shows the denatured ampholyte to have a crystallinity like that of fibrous proteins, the degree of which increases at high temp. during several hours. A copolymer of aminostyrene and maleic acid behaves similarly. H.H.H.

Urea-Formaldehyde Condensations. XVIII—Butylation of the Condensates

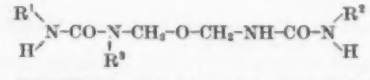
G. Zigeuner and H. Fitz

Mh. Chem., **90**, 211–221 (21 April 1959)

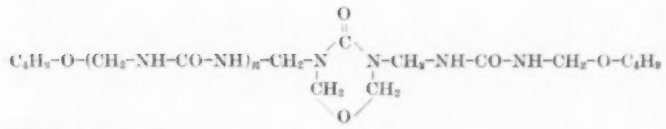
Processes which occur during the hardening of urea methylols and also in the formation of butylated urea–formaldehyde resins are investigated by means of paper chromatography, whereby important conclusions are drawn with respect to the homogeneity of individual condensates. The formation of the above resins would appear to occur via urea methylols (I) and biscarbamido methyl ethers (II), which, in acid media, undergo a complex reaction into urea condensates (III) from which de-etherification with expulsion of butoxy residues ensues.



(I: $R^1=R^2=R^3=H$, $R^4=CH_2OH$; or $R^1=R^2=H$, $R^3=R^4=CH_2OH$)



(II: $R^1=CH_2OH$, $R^2=R^3=H$; or $R^1=R^2=CH_2OH$, $R^3=H$; or $R^1=R^2=R^3=CH_2OH$)



(III: $n=0$ or $n=1$.)

H.H.H.

Polyampholyte with "Built-in Dye"
M. L. Bhaskara Rao and S. R. Palit
Proc. Chem. Soc., 223 (Aug. 1959)

The polymer-dye obtained by coupling the diazotised copolymer of aminostyrene and methacrylic acid (see preceding abstract) with -hydroxynaphthalene-2,7-disulphonic acid, is sol. in ac ' and in alkali, but if the diazotisation is incomplete, ' wing a polyampholyte, the dye can be pptd. by additic of acid. This pptn. occurs after a time-lag and the ppt. cannot be dissolved in alkali, an insolubilisation akin to denaturation except that it is more rapid. In the dye-polymer, a large number of dye units are attached to the polymer chain by non-conjugative bonds, which results in many single chromophoric systems. The carboxylic and sulphonic acid groups render the polymer water-soluble and intensify the colour. The spectral characteristics are little affected by changes of pH, they indicate wide deviation from the Beer–Lambert law, and the continuous decrease in light absorption with increasing concn. of dye is comparable to the self-quenching of fluorescence; metachromacy seems to be a kindred phenomena. H.H.H.

States of Aggregation of Highmolecular Compounds. III— Synthetic Polyamides
R. I. Fel'dman
Kolloid. zhur., 21, 238–243 (March–April 1959)

The effect of heating and cooling on capron and nylon (fibre, rod, and film) have been investigated using the techniques of linear dilatometry. It is found that the length–temp. dependence is normal for rod shaped samples but rather complex for films and fibres due to (*a*) the directional effect in the coefficients of linear expansion; (*b*) anomalous shrinking (both volume and length) with increase in temp. over certain temp. intervals due to the transition from the unstable non-equilibrium state to a more stable state; (*c*) shrinking caused by a change in the degree of orientation of anisotropic materials; (*d*) the process of "autocatalytic" moisture uptake over the temp. interval 20–40°C. G.J.K.

Preparation and Properties of Lyophobic Colloids of Fibre Forming Polymers
N. V. Mikhailov, V. I. Maĭboroda, and S. S. Nikolaeva
Kolloid. zhur., 21, 246–247 (March–April 1959)

The preparation of colloidal soln. of polyethyleneterephthalate (concn. 4·5%) and polycaprolactam (concn. 2%) is described and the physico-chemical properties of the obtained sols (I) are tabulated. Electro-microscopic investigation has shown I to be globular (500–1,000A.) and capable of forming chain aggregates. G.J.K.

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Tetrakis Hydroxymethyl Phosphonium Chloride as Colour Stabiliser for Acrylonitrile Polymers (VI p. 624)

XIV— ANALYSIS; TESTING; APPARATUS

Determination of Ionic Surface-active Agents with Dyes
M. Aoki and Y. Iwayama

I— Erythrosin (C.I. Acid Red 51) and Eosin (C.I. Acid Red 87) Methods
Yakugaku Zasshi, 79, 522–526 (1959)

Alkyl sulphate or alkylarylsulphonate (5–20 mg.) is titrated with 0·005M-cationic surface-active agent in buffer solution at pH 4·5 in presence of $CHCl_3$ using erythrosin as indicator. The endpoint is shown by the $CHCl_3$ layer becoming crimson. The error is $\leqslant 0{\cdot}2\%$. The method can be applied to the analysis of various types of invert soap and long-chain aliphatic amines. Eosin and Erythrosin in a concentration range of 3×10^{-6}–3×10^{-5}M can be used as the indicator with invert soaps.

II— Toluidine Blue (C.I. 63340) Method
Chem. Abs., 53, 16562 (10 Sept. 1959)

In a two-phase titration using anionic surface-active agent as titrant, Toluidine Blue was the best indicator. Titrating a solution at pH 8 in presence of $CHCl_3$ with Toluidine Blue as indicator results in the $CHCl_3$ layer changing from crimson to blue to mark the endpoint. Using 0·005M-anionic surface-active agent as titrant, 5–20 mg. of cationic surface-active agent can be determined with an error of $\pm0{\cdot}2\%$ or less. Toluidine Blue can be used as a reagent for colorimetric determination of anionic surface-active agents in a concentration range of 1×10^{-6} $-1{\cdot}5\times10^{-3}$M. C.O.C.

Titration of Triphenylmethane Dyes with Vanadium. II— Sulphate in Presence of Sodium Xylenesulphonate
M. Matrka and Z. Sagner
Chem. Průmysl. 8, (33), 22–24 (1958): *Chem. Abs.*, 53, 16797 (25 Sept. 1959)

0·1 N-VSO_4 was used, VSO_4 (12·0 g.) was dissolved in N-H_2SO_4 (1 litre) and the solution reduced with Zn amalgam or Zn. Basic dye (0·3–0·4 g.) was dissolved in water (100 ml.) or acid dye (0·6–1·0 g.) in 15% Na xylene sulphonate (100 ml.); 50 ml. of a saturated solution of Rochelle salt, Na citrate, or acid sodium tartrate, was added to the latter. The solution was titrated at 50°C. in an atmosphere of nitrogen. The method gave better results than titration with $TiCl_3$. C.O.C.

Iodometric Determination of Zinc in Ammonium Bifluoride Buffer Medium. Rapid Estimation of Total Zinc Oxide (C.I. Pigment White 7) in Mixed Paint Pigments
K. C. Seal *Indian J. Appl. Chem.*, 21, 125–8 (1958): *Chem. Abs.*, 53, 16555 (10 Sept. 1959)

Add ammonia (1 : 1) dropwise to an aliquot of Zn solution in a 500 ml. conical flask until blue to litmus paper. Cool, add $(NH_4)HF_2$ (2–3 g.), KI (3 g.) and dilute with water to 250 ml. Add 0·1M-ferricyanide in 5 ml. excess. Shake and keep in the dark for 2–3 min. Titrate with standard $Na_2S_2O_3$ to a starch endpoint. To calculate the ZnO in the solution multiply the stoichiometrically calculated amount of ZnO by the empirical factor 1·020. Moderate concentrations of Fe^{3+}, Pb^{2+} and Cr^{3+} do not interfere. Procedure for preparing the test solution from pigments whose ZnO content is to be ascertained is described. C.O.C.

Identification of Man-made Fibres
P.-A. Koch *Textil-Rund.*, 14, 438–445 (Aug. 1959)

A series of tables based on microscopical examination, particularly of cross-sections and on specific reactions of the fibres, mostly solubilities. S.R.C.

Use of Procion Black HGS (ICI) as a Stain for Differentiation of the Skin and Core of Viscose Rayon Fibres
K. Kato *J. Soc. Textile Cellulose Ind. Japan*, 15, 494–498 (June 1959)

Applied with urea and soda ash Procion Black HGS is selective for skin and needs no particular differentiation procedure. With wool bilateral staining occurs while with Vinylon the skin is selectively stained. C.O.C.

Wool Damage— Topochemical Evidence
K. Tomopulos and R. Ritter
Melliand Textilber., 40, 676–677 (June 1959)

The technique of applying the Pauly reaction for localised damage in wool is improved. Contacting single fibres on the microscope slide first with an aq. soln. of benzenesulphonic acid diazonium salt and only then with 5–10% Na_2CO_3 gives sharply defined coloured coupling products in damaged zones only. If a LiBr soln. of the diazonium salt is used, higher concn. are possible, giving greater contrast, and stability for storing for at least 6 weeks is obtained. The test shows up alkali damage particularly well, also on a macro-scale. S.M.J.

Cystine Analysis in the Investigation of Complaints
W. Schönberger *Textil Praxis*, **14**, 600–606 (June 1959)

Wool is hydrolysed with HCl or H_2SO_4. Addition of $NaHSO_3$ converts cystine into cystein which is oxidised with $H_6P_2O_8(WO_3)_{18}$ (Folin's reagent) into a blue coloured complex, suitable for colorimetric estimation. Although changes in the cystine content of wool caused by chemical reagents, light, steam, etc. are useful criteria of the degree of modification of the fibre, more conclusive evidence is obtained if other quantitative tests such as alkali solubility are carried out to supplement cystine analysis.
L.A.T.

Qualitative Test for Cystein based on a Photographic Method
F. H. Schwarzenbach
Helv. chim. Acta, **42**, 1133–1141 (15 June 1959)

It is found that when drops of a soln. of cystein react with the sensitive layer of a photographic emulsion, the film, after exposure and subsequent development, will exhibit the presence of cystein as bright specks on the dark background. The test is suitable for the detection of cystein in soln. or for its localisation in filter paper (chromatograms, electropherograms, etc.), and in particular for its distinction from the sulphur containing amino-acids cystein and methionin. The test limits for cystein in soln. at pH 4·0 are drops of 0·04 ml. of concn. 6 mg./l., i.e. for an absolute amount of 0·24 μg. The chemistry of the photographic reaction is still unexplained but a free SH-group appears to be necessary. H.H.H.

Simple Method of Determining the Degree of Setting of Polyamide and Polyester Fibres
K. Schwertassek
Faserforsch. und Textiltech., **10**, 387–392 (Aug. 1959)

The temperature is determined at which the fibre dissolves in sulphuric acid of a certain concentration in 3–4 and 4–5 seconds. Application of the method to polyamide and polyester fibres is described. The method is simple and suitable for works control. W.R.M.

Simple Method of obtaining Diffusion Coefficients of Dye in Fibre
H. Uedaira
J. Soc. Textile Cellulose Ind. Japan, **14**, 481–483 (July 1958)

For both infinite and finite dyebaths (Dt/r^2) is expanded as a power series of M_t/M_∞ where D is the diffusion coefficient, r the radius of the fibre M_t the amount of dye taken up by the fibre in time t, and M_∞ the amount taken up at equilibrium.

Thus $y = x + Ax^2 + Bx^3 + Cx^4 \ldots$

where $A = \frac{\pi^{\frac{1}{2}}}{2}\left(\frac{1}{2} + \frac{2}{a}\right)$

$$B = \frac{2}{3}\left(\frac{1}{8} - \frac{2}{a} - \frac{4}{a^2}\right) + \frac{\pi}{2}\left(\frac{1}{2} + \frac{2}{a}\right)^2$$

$$C = \frac{5\pi^{3/2}}{8}\left(\frac{1}{2} + \frac{2}{a}\right)^3 + \frac{5\pi^{\frac{1}{2}}}{3}\left(\frac{1}{2} + \frac{2}{a}\right)\left(\frac{1}{8} - \frac{2}{a} - \frac{4}{a^2}\right) + \frac{\pi^{\frac{1}{2}}}{4}\left(\frac{1}{8} + \frac{3}{2a^2} + \frac{8}{a^3}\right)$$

and $y = \left(\frac{Dt}{r^2}\right)^{\frac{1}{2}}$, $x = \left(\frac{\pi^{\frac{1}{2}}}{4}\right)\left(\frac{a}{1+a}\right)\left(\frac{M_t}{M_\infty}\right)$

For an infinite dyebath this simplifies to

$$y = x + 0{\cdot}44311\,x^2 + 0{\cdot}47603\,x^3 + 0{\cdot}67513\,x^4$$

L.P.

Colour Preference and Subjective Colour Structure
R. Hefner and J. Zinnes
Off. Dig. Fed. Paint Varn. Prod. Cl., **31**, 1030–1048 (Aug. 1959)

A report of study carried out at the University of Michigan to provide basic information about the nature of preference judgments — how preferences are related to psychological colour-order systems, how preferences change over time, how they differ for different objects, and when different numbers of colours are available to be chosen. The work is being carried out under conditions which make it possible to specify completely the characteristics of the colours, lighting, and observers, that might influence the results. Colour workers already differentiate between psychophysical and psychological colour systems, and colorant mixture systems; a new colour-order system, a colour preference space, is now postulated. Three theories of preference are outlined and compared.
J.W.D.

Determination of Polymer Compositions in Dye Solutions by means of Absorption and Luminescence Centres
Izvest. Akad. Nauk S.S.S.R., Ser. Fiz., **23**, 70–73 (1959): *Chem. Abs.*, **53**, 11990 (10 July 1959)

The polymer concentration, x, can be derived from the equations $(c-mx)^m/x = k$ and $D = \varepsilon x l + \varepsilon_0(c-mx)l$, ($c$ = total concentration of the substance; k = equilibrium constant; ε and ε_0 = absorption coefficients of the monomer and the polymer, D = optical density; l = thickness of the absorbing layer). x can be calculated from measurements at three concentrations. Such measurements were made on aqueous solutions of Rhodamine 6G (C.I. Basic Red 1). An attempt was made to calculate the concentration of polymers by using further derived formulae for the decrease in luminescence caused by presence of non-luminescent polymers. The attempt with C.I. Basic Red 1 failed because quenching is also caused by migration of energy. C.O.C.

Fuchsine (C.I. Basic Violet 14) for Identifying Nylon
K. Ito *Kógyó Kagaku Zasshi*, **60**, 1207–1208 (1957): *Chem. Abs.*, **53**, 12685 (10 July 1959)

C.I. Basic Violet 14 (0·05 g.) is dissolved in water (200 c.c.) and 6 N-NaOH (10 c.c.) and the red precipitate filtered off after 10 min. Nylon 6 or 66 boiled in this solution for 5 min. bec[illegible]s red whereas poly(vinyl alcohol) fibres, acetate, wool, silk, cotton, and hemp remain unstained. C.O.C.

Red Lead Paints and the Rapid Evaluation of their Anticorrosive Properties
Z. Klonowski and M. Knopf
Przemysł Chem., **12(35)**, 43–47, 151–167 (1956): *Chem. Abs.*, **53**, 7619 (25 April 1959)

Reflectivity of a Mixture of White and Black Powders
H. Kuno and S. Hayakawa
Proc. Fujihara Man. Fac. Eng., Keio Univ. (Tokyo), **10**, (30), 17–25 (1957): *Chem. Abs.*, **53**, 8769 (25 May 1959)

Relative reflectivity R_p taken as 1·0 for the white powder and 0 for the black was given by $R_p = (1-p)/(1+L_p)$ (p = apparent vol. fraction of the black powder in the mixture; L = a constant characteristic of a pair of white and black powders). Effects of the particle size distribution of the white powder on the reflectivity of the mixed white and black powders showed that the reflectivity is the sum of that of the various components of the white powder. The relationship between the constant L for a white powder and the corresponding constants for mixture of the white with the same black powder were calculated and the results confirmed by experiment. C.O.C.

Improved Method of Hiding Power Determination
W. S. Van Eyken and F. T. Anderson
Am. Paint. J., **43**, (31), 78–95 (1959): *Chem. Abs.*, **53**, 14537 (10 July 1959)

The test paint is applied to a hiding-power chart by a multinotch drawn-down blade applying many thicknesses of paint simultaneously. Reflectance ratios are determined on the black and white sections of the chart at each paint thickness and sections of the painted paper are weighed to determine the amount of paint applied. Percentage contrast ratio is then plotted against the respective dry opacities expressed in sq.ft./gal. C.O.C.

Silver Staining Method for Rayon Cross-sections
K. Kato *Text. Research J.*, **29**, 409–415 (May 1959)

A technique using $AgNO_3$ soln. gives results generally corresponding to those obtained by the usual method employing normal dyes. The staining, however, proceeds in a quite different manner from the dyeing methods. Several rayons were examined and a number of factors evaluated regarding their influences on the silver staining.
S.B.D.

XV—MISCELLANEOUS

Isolation of Berberine (C.I. 75160) from the Roots of *Berberis vulgaris* and its Chromatographic Testing (IV p. 617)

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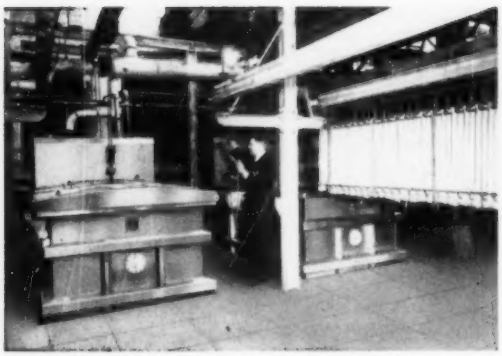

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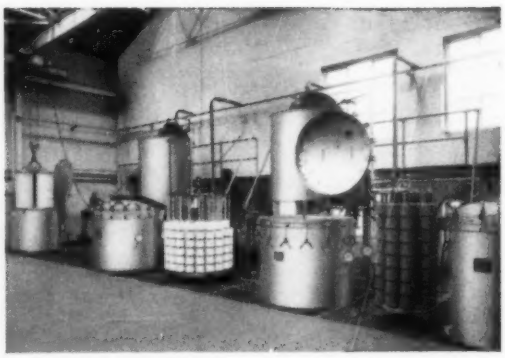

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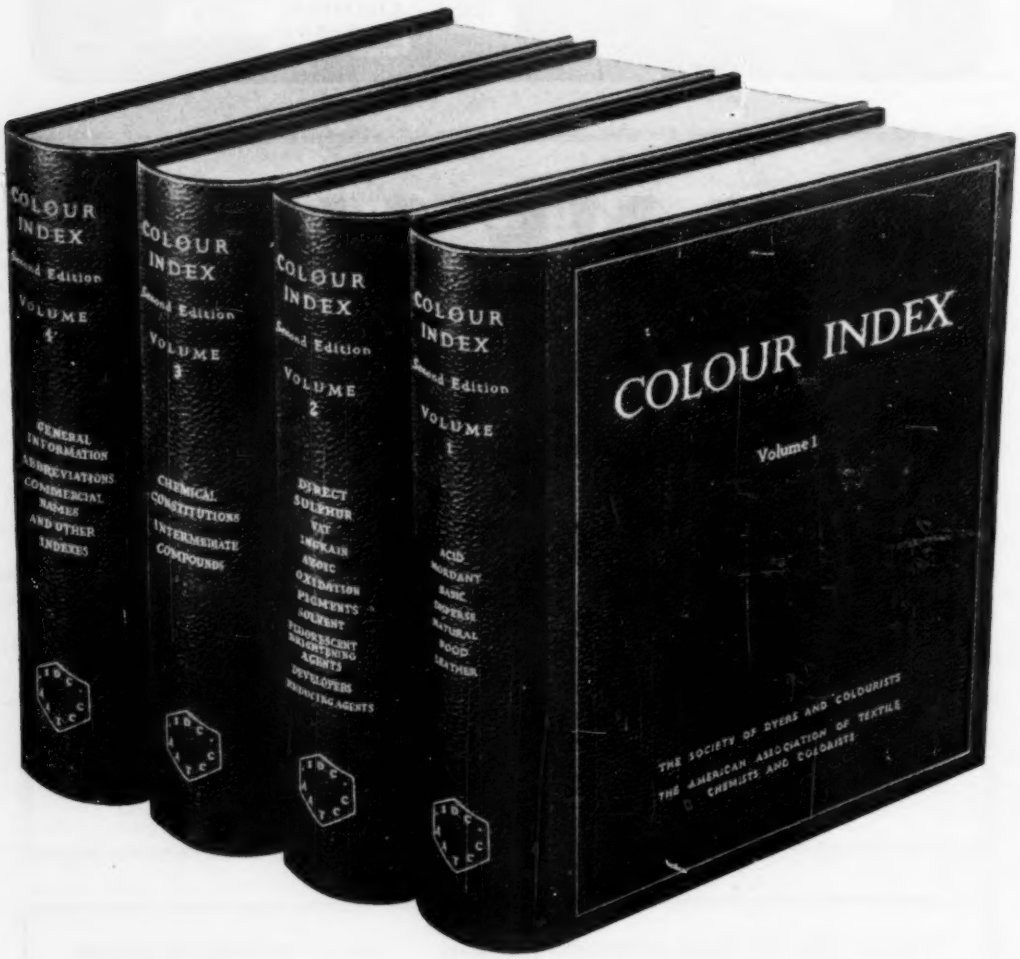

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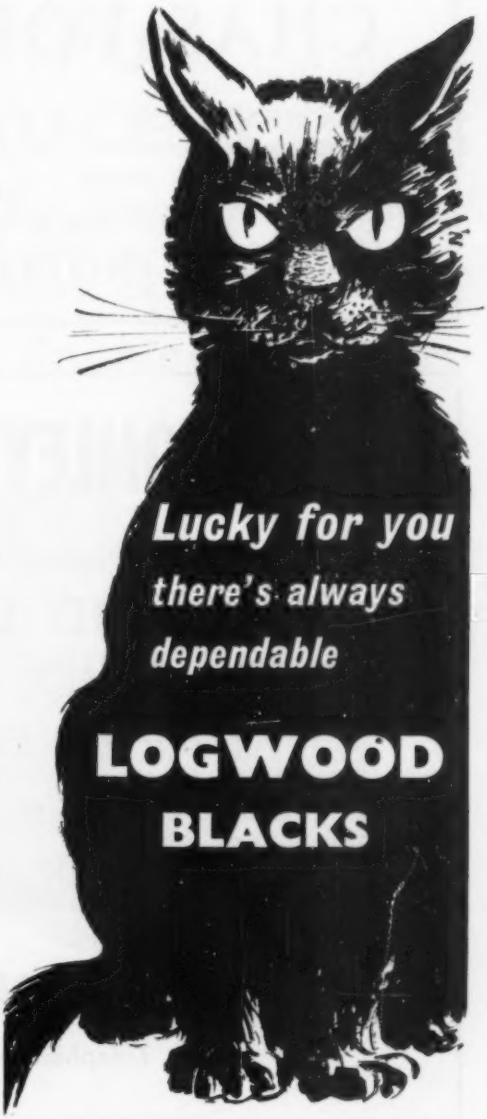

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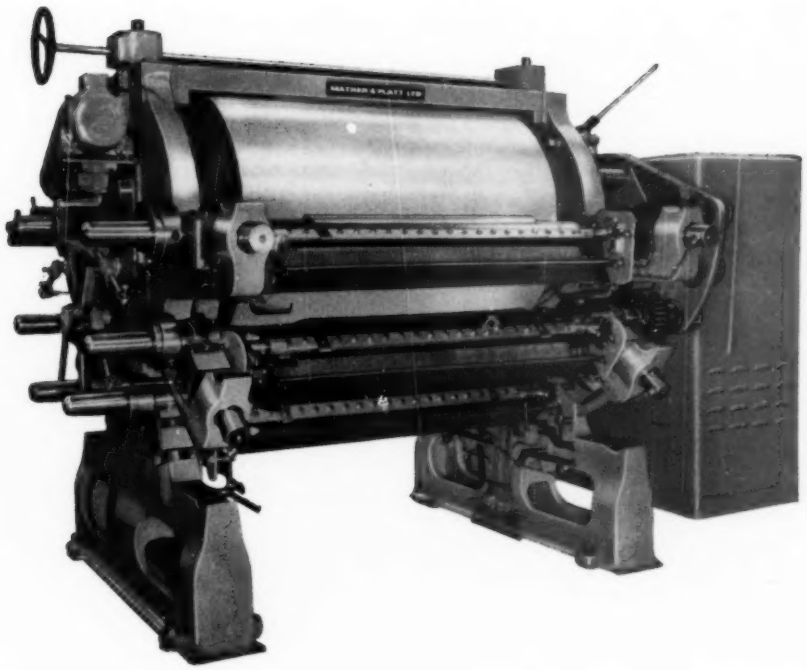

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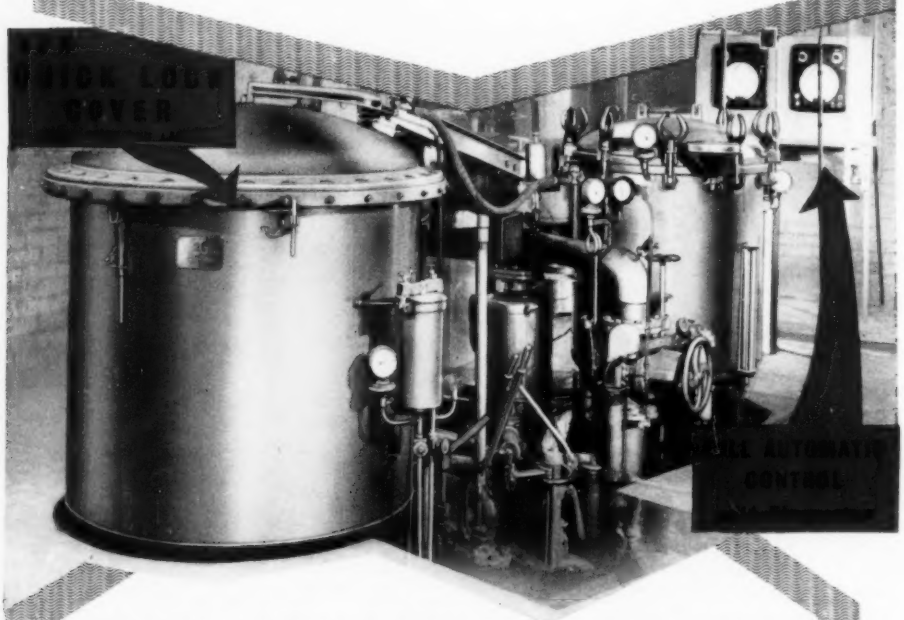

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